

SYNTHESIS AND ACID LEACHING
OF BRANNERITE, UTi_2O_6

by

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A Thesis submitted for the degree of
Doctor of Philosophy of the University
of London and for the Diploma of
Membership of Imperial College.

November 1981

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To my parents

ABSTRACT

A review of natural brannerite occurrences and current leaching practice on brannerite-containing ores is given.

Reports of brannerite synthesis are collated and attempts made to repeat the various methods described. A pure brannerite sinter has been successfully synthesised from uranium and titanium dioxides by a solid-state pyrosynthesis; melting techniques proved unsuccessful.

A fundamental study of the behaviour of the synthetic brannerite under acid leaching conditions has been made and the influence of the important leach variables (acid type and concentration, temperature, particle size, oxidant presence and pre-baking) determined. The effects of these leach variables are explained in terms of proposed dissolution mechanisms. Dissolution of brannerite is shown to occur only under conditions of high acid concentration, high temperature and high oxidation potential. Activation energy measurements and leach model fitting indicate mixed diffusional and chemical control with the actual mechanism dependent on temperature and oxidant. The influence of sinter structure on leaching is discussed.

A doped brannerite was synthesised, with iron (added as Fe_2O_3) replacing uranium. The change in fundamental leaching characteristics on acid leaching is interpreted in terms of chemical and structural changes on doping. The doping addition is found to reduce leachability.

A natural brannerite-containing ore from Elliot Lake, Ontario has been acid leached and the results interpreted in terms of the ore mineralogy.

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INTRODUCTION

In the early seventies the Arab oil embargo and the four-fold increase in world oil prices led to the decision by many countries to expand their nuclear energy programmes. Many emergency measures were undertaken, including stockpiling of uranium, with the result that there was insufficient on the world market to satisfy all the demands. Long term sales were agreed and, for example, Canada was committed to sell ten times its annual production. The overall effect, taking all the market factors into account, was a dramatic increase in the price of the raw product for nuclear power production, U_3O_8 .⁽¹⁾

For the uranium-mining industry, the increased prices made more operations viable and led to efforts of greater utilisation of lower grade ores than had previously been processed, and ores other than the traditional pitchblendes. Typically these were the carbonaceous materials, such as thucholite (fine dispersion of uraninite in hydrocarbons) and some of the more refractory, multiple oxide ores.

Brannerite, a complex uranium titanate, which contains more uranium than any other U-mineral except the pitchblendes (typically 30-40%), is one of the major constituents of many of the ore-bodies in the Elliot Lake region of Ontario. Typical deposits in this area contain ~0.1%U which apparently make them viable for commercial exploitation. However, the highly refractory nature of brannerite has prevented full utilisation of the source and typically only 30-50% of the uranium can be extracted by several hours leaching in boiling 40% acid. A further complicating factor is that, not only does brannerite have a wide range of chemical compositions, but it also appears to undergo varying degrees of weathering (oxidation) and it seems likely that the major uranium extraction is from the altered mineral rather than the pure form. It is clear

that a full understanding of the required leach process variables and their action on brannerite is lacking.

In the present study, a fundamental investigation of the leaching characteristics of brannerite has been undertaken, the first step having been the synthesis of a pure, unweathered mineral. The aim is to provide data and an understanding of the dissolution behaviour of UTi_2O_6 (pure brannerite) under the normal leaching variables of temperature, acid concentration, particle size and oxidant presence and to relate this to the influence of impurity elements and weathering of the natural form.

SECTION 1
LITERATURE SURVEY

1.1. NATURAL BRANNERITE

1.1.1. Occurrences of Natural Brannerite

The locations and modes of occurrence of natural brannerite deposits are shown in Table 1.

1.1.2. Mode of Formation of Natural Brannerite

The limited literature available on the formation of natural brannerite shows a division of theories between hydrothermal and pegmatitic mechanisms. Ramdohr⁽¹⁰⁾, in one of the earliest references, reported brannerite at the Pronto Mine in the Blind River region of Ontario. Examination of the brannerite conglomerates suggested that the formation reaction was apparently pseudomorphic with the growth of the uranium titanate on titanium minerals or uraninite. This hydrothermal reaction was assumed to have taken place by an additive process between 2TiO_2 and UO_2 under unknown conditions of temperature and pressure. This type of reaction was termed the "Pronto-Reaction" after the original observation.

Evidence cited for the validity of a hydrothermal mechanism was summarised as three observations of the mineral⁽¹¹⁾:

- by the nature of brannerite originating at the expense of uraninite and more particularly rutile, minute exsolved grains of TiO_2 were almost always visible and brannerite growth from the outside to the centre of the TiO_2 aggregates resulted in coarse crystals which decreased in size towards the periphery,

Table 1, Occurrences of Natural Brannerite

COUNTRY	LOCATION	ORE TYPE	OTHER INFORMATION	REFERENCES
CANADA	Blind River/Elliot Lake, Ontario. The four locations in Blind River are 1. Pronto uranium mines in Long Township. 2. Algom uranium mines near Quirke Lake. 3. Lot 8, concession V, Baldwin Township. 4. Lot 10, concession VI, Drury Township.	Quartz-pebble conglomerate reefs and quartzite (known as "Mississagi quartzite") strata. Distributed in large, uniform and continuous deposits (e.g. Pronto mine has an ore-body of length 3800-7500' and consistent thickness of 8-13'. Veins found to a depth of 2000'). The quartzite containing the ore-bearing crystals is characteristically cross-bedded and green coloured. Shows some indication of placer origin.	1. The largest reserves of uranium in Canada and the most important deposit of brannerite. Other, lesser, minerals are uraninite, monazite, pitchblende and thorogummite (an alteration product of brannerite). 2. Found as microscopic grains ($\sim 100 \mu\text{m}$ diameter) in a matrix of conglomerate. The conglomerate consists of rounded, well-packed, quartz pebbles averaging $\frac{1}{4}$"-2" in size. They are of a glassy, milky-white and smoky-grey variety with lesser black cherts, red jasper and feldspar. The matrix consists of sericite, chlorite, granular quartz, white mica, biotite, rutile and mainly pyrite. 3. Average 0.10-0.15% U_3O_8 (= 2-2.5 lb U_3O_8 per ton). 4. Pyrite abundant (3-5%) and other sulphides noted; confined almost entirely to matrix. 5. Silica content of ore is >75%. 6. S.G. of ore is 2.7-3.0.	(2), (3), (4), (5)
	Bancroft, Ontario. Foster Lake, Beaver-lodge Lake, Sask.. Great Bear Lake, N.W.T.	As Elliot Lake.		(2), (4)
U.S.A.	Stanley Basin, Idaho.	Gold placers, grains of prismatic tendency.	Highly radioactive.	(6)
	Kelley Gulch, Western Custer Co., Idaho.	Granite cut by pegmatites. Grains of prismatic tendency and rounded detrital pebbles. Also gold-bearing alluvial deposits.	Highly radioactive; mineral probably in pegmatite. Minor constituent of deposit.	(5), (6), (7), (8)

... Continued ...

Table 1, (continued)

COUNTRY	LOCATION	ORE TYPE	OTHER INFORMATION	REFERENCES
U.S.A. (Cont'd)	West Walker River, Mono Co., California. California Mine, Chaffee Co., Colorado. Rainy Mine, King Co., Wash. Penn Haven Junction, Carbon Co., Pa.	All quartz veins.	All trace constituent.	(4), (5)
AUSTRALIA	Mary Kathleen Deposit, near Mt. Isa, Queensland.	Mainly garnet-rich rock found with granitic rocks.	Secondary to pitchblende in allanite.	(2)
	Crockers Wells, Radium Hill, South Australia.	Complex iron-titanium veins in granitic breccia rocks. Some evidence of quartz veins.	Processing difficult and expensive. Davidite ($U_6Ti_{15}(OH)_3$) also present. Also occurs as a high thorium variety of brannerite, absite. Associated with rutile, zircon, xenotime and apatite. Readily recovered by flotation.	(2), (3)
	South Alligator River areas of Northern Territory.	Several deposits in recent and large discoveries. Vein-type deposit.	Associated with pitchblende and davidite. Ore grade is generally higher than other uranium mineral areas, but processing is more difficult.	(1)
SOUTH AFRICA	Witwatersrand.	Rare titaniferous grains in quartz-pebble conglomerates.	Only tentatively identified whilst (5) declares it absent. (9) suggests that it was once widespread but had undergone alteration to secondary uraninite. Associated with pyrite, thucholite, quartz and gold.	(4), (5), (9)

... Continued ...

Table 1, (continued)

COUNTRY	LOCATION	ORE TYPE	OTHER INFORMATION	REFERENCES
PAKISTAN	Udaisage, Udaipurish Districts.			(4)
THAILAND	Phuket-Phangnga Region	Discard from tin-mining operations.	Secondary to monazite and euxenite. Also present is samarskite. Th:U ratio ~ 1 .	(9)
FRANCE	Chateau-Lambert, Vosges.	Quartz veins.	Found with molybdenite and uraninite as a rare and localised constituent.	(4), (5)
SPAIN	Fuenteovejuna, Cordoba.	Pegmatite	Known locally as cordobaite	(4)
MOROCCO	Bou-Azzer Mine.			(4)

- newly formed brannerite was commonly associated with small tablets of pyrrhotite,
- a reversed formation of brannerite to an unusual "secondary" uraninite and TiO_2 , known as "weathering" or "altering", occurred resulting in small, jagged, elongated grains of uraninite.

It has been suggested⁽¹²⁾ that the brannerite of Blind River was deposited as a detrital mineral and that after consolidation of the sediments, weathering occurred via hydrothermal solutions (emanating from granitic rocks) permeating the conglomerates, depositing pyrites, and altering brannerite to uraninite. Such a proposal was used to explain the presence of altered brannerite in the Witwatersrand area of South Africa.

At least one of the above observations has been used to explain the presence of hydrothermal brannerite in the mines of the Dominion Reef and at Bou Azzer⁽¹¹⁾.

However, brannerite from other parts of the world, notably Idaho, Mono County, Cordoba, Queensland, and some localised areas of Blind River showed none of the above characteristics. The quartz-like appearance was more consistent with a pegmatitic mode of formation from granitic magma⁽⁵⁾. Holmes⁽¹³⁾ has collected the reports of pegmatitic brannerite and categorised them as having occurred in pyrite-bearing conglomerates, placers, granitic and dioritic rock and in quartz dikes of pegmatitic or metamorphic derivation.

Clearly, the mode of brannerite formation is far from having been settled and there remains the possibility that both modes were operative, dependent on location.

1.1.3. Physical Characteristics of Natural Brannerite

Natural brannerite is a radioactive mineral which exhibits a tendency towards prismatic grains⁽⁶⁾. Unweathered mineral is jet black but altered brannerite is characterised by a variety of colours ranging from colourless/white-grey through green/yellow to reddish brown^{(6),(11),(14)}. The mineral is opaque, but thin slivers are transparent allowing the transmission of yellow/green light⁽⁶⁾. Fresh brannerite displays a resinous lustre but is non-fluorescent⁽⁴⁾. Thin section autoradiographs show the mineral to be optically isotropic with indices $n_{\text{Li}} = 2.26 \pm 0.02$ and $n_{\text{Na}} = 2.30 \pm 0.02$ ⁽⁵⁾.

The mineral is exceedingly brittle, particularly at grain boundaries and cracks⁽¹¹⁾, with fracture being conchoidal and exhibiting no evidence of cleavage⁽⁶⁾. Typically, the hardness varies from 4.5 to 6.5 and specific gravity from 4.2 to 5.8⁽⁴⁾. The higher S.G. forms seem to be the most radioactive. Brannerite is generally metamict⁽⁷⁾, see Section 1.1.5., and apparently homogeneous, although there is evidence of minute surface cracking⁽⁶⁾.

1.1.4. Chemical Characteristics of Natural Brannerite

The polyvalence of uranium and the relatively high solubility of the hexavalent form in water has two major effects; it allows a large number of minerals and it permits a wide variation of chemical composition within each mineral group. Brannerite is classified under the umbrella of complex multiple oxides of uranium and more specifically, as one of the complex titanates. These oxides contain a variety of elements having similar valencies and ionic radii which may interchange with each other within the crystal lattice⁽²⁾.

The idealised formula of brannerite is UTi_2O_6 where, in part, U can be replaced by Ca, Th, Fe, Y and other transition metals and Ti by Fe(III). An approximate analysis of a natural deposit gave a breakdown of:

UO_2 up to 29%	$H_2O = 0.3 - 10\%$
UO_3 up to 42%	+trace amounts of many elements
$TiO_2 = 31 - 43\%$	
ThO_2 up to 8%	Typically U:Th = 10:1
$CaO = 1.1 - 3.45\%$	
Fe_2O_3 up to 4%	

The H_2O was probably due to the presence of alteration products⁽⁸⁾.

The uranium content of brannerite can vary between 27% and 55% when pure and so brannerite contains more uranium than any other mineral except the pitchblendes⁽⁶⁾.

Brannerite has been shown to undergo a weathering reaction in which some of the U(IV) is oxidised to U(VI) with the resultant exsolution of TiO_2 which is usually exhibited as anatase. The uranium products of alteration are secondary uraninite or thorogummite, a complex silicate/hydroxide. Enrichment of the thorium content has also been noted⁽⁵⁾.

The mineral is reported to decompose in hot HNO_3 and concentrated H_2SO_4 , but is insoluble in aqua regia⁽⁸⁾.

1.1.5. Metamict Brannerite

Brannerite, like many other uranium-containing minerals, exhibits the property of being metamict to varying degrees. The term is used to describe an originally crystalline material which, in the course of

time, has assumed the properties of an amorphous substance due to lattice disruption by radiation damage, without change in original crystal form. The damage is generally regarded as being caused by alpha particle bombardment.

The properties of metamict minerals can be summarised by the following observations:

- optically isotropic,
- pyrognomic, readily becomes incandescent on heating,
- lacking in cleavage, fracture conchoidal,
- density lowered on becoming metamict,
- crystal structure reconstituted on heating,
- resistance to attack by acid increased by heating,
- contains U or Th at levels greater than 0.5% U_3O_8 and/or ThO_2 ,
- minerals can exhibit a range of metamict/crystalline states,
- X-ray amorphous,
- minerals show little or no hydration.

Examination of metamict brannerite from Idaho has shown that heating produces two kinds of cryptocrystalline materials, the grains of which can be distinguished by external features. It was presumed that one kind corresponded to the heating product of simple metamict brannerite and the other had, in addition, suffered some chemical change whilst remaining in the metamict state^{(15), (16)}.

The degree to which a mineral has become metamict is expected to have an effect on the mineral leachability by virtue of having disrupted the crystal lattice and it is suspected that the amorphous material will be dissolved preferentially to fully crystalline structures. No leaching tests, to the author's knowledge, have been carried out to investigate this phenomenon.

1.2. ACID LEACHING OF URANIUM

1.2.1. Choice of Acid

Leaching, to extract metal values from an ore, involves the selection of a range of pH and oxidation potential over which a metal-containing ion is stable in solution whilst the mineral source is unstable. It has long been known that uranium can be solubilised under both acid and alkaline conditions, providing that the exact conditions are chosen correctly. Langmuir⁽¹⁷⁾ and more recently Burkin⁽¹⁾ have correlated many sources of thermodynamic considerations of uranium in solution to explain this well-known phenomenon.

The choice between acid and alkali leaching of a uranium deposit depends, in part, on the physical characteristics of the ore such as, the type of uranium mineralisation, ease of liberation and the nature of other constituent minerals present. For example, if an ore-body contains a significant amount of carbonates and other bases, acid leaching would result in a large wasted consumption of acid. Carbonate leaching is ineffective for silicate-type uranium minerals, uranium minerals containing U(IV) and highly refractory minerals of the multiple oxide group, since intensive treatment with oxidation and long residence times at high temperature are required before significant extractions are achieved⁽²⁾.

In deposits such as Elliot Lake, Ontario brannerite is contained in ore in which the gangue is >75% silica. Thus, acid leaching provides the only viable extraction procedure.

Acid leaching of uranium minerals nearly always refers to the use of sulphuric acid. Sulphuric acid is advantageous in comparison to the other common acids for the following reasons:

- nitric acid has strong oxidising properties, but is expensive and uranyl nitrates, in dilute solution, are incompatible with anion-type ion exchange,
- hydrochloric acid is expensive, highly corrosive and can only be successfully used when the acid can be recovered (for example, in salt roasting processes when the acid is recovered from roaster gases).

1.2.2. Chemistry of Acid Leaching

The chemistry of acid leaching of uranium is well established and documented and so it will not be dealt with to any great depth here. An interested reader is recommended to refer to a recent review by Langmuir⁽¹⁷⁾ in which uranium solution - mineral equilibria are considered.

Uranium minerals subjected to acid leaching generally contain uranium in the tetravalent and hexavalent states. In an E_H -pH diagram showing the relative importance of the +4 and +6 valent uranium species in solution, Langmuir⁽¹⁷⁾ has demonstrated that the +4 valency state is only stable in solution (as U^{4+}) under highly acidic and low oxidation potential conditions whereas U^{6+} , existing as the uranyl ion UO_2^{2+} , occupies a much larger range of stability - Figure 1.

The practical outcome of the thermodynamic situation is that an oxidising agent is necessary to cause minerals containing U(IV) to react and dissolve under normal acid leaching conditions. The uranyl minerals do not require an oxidising agent.⁽¹⁾

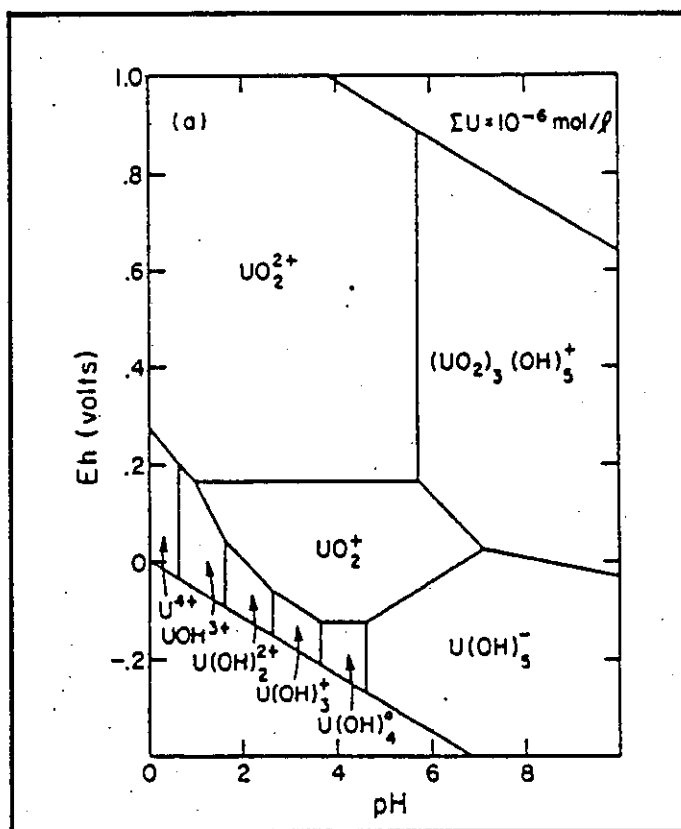
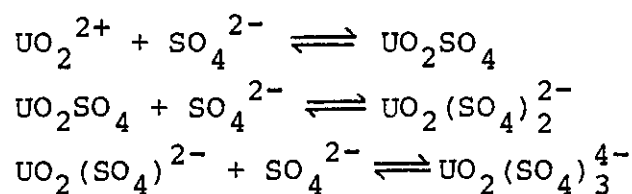


Figure 1, E_h -pH diagram showing the relative importance of +4, +5 (as UO_2^+) and +6 valent uranium species at 25°C for $\Sigma U = 10^{-6} M$ (after Langmuir⁽¹⁷⁾)

Sulphuric acid leaching introduces into solution the sulphate, bisulphate and hydrogen ion. Reactions of these ions with the uranyl ion can be summarised by the following equilibria.



The stability of the above complexes are most easily represented by introducing sulphur into the U-H₂O E_h -pH diagram to form a Pourbaix Diagram of the form of Figure 2.

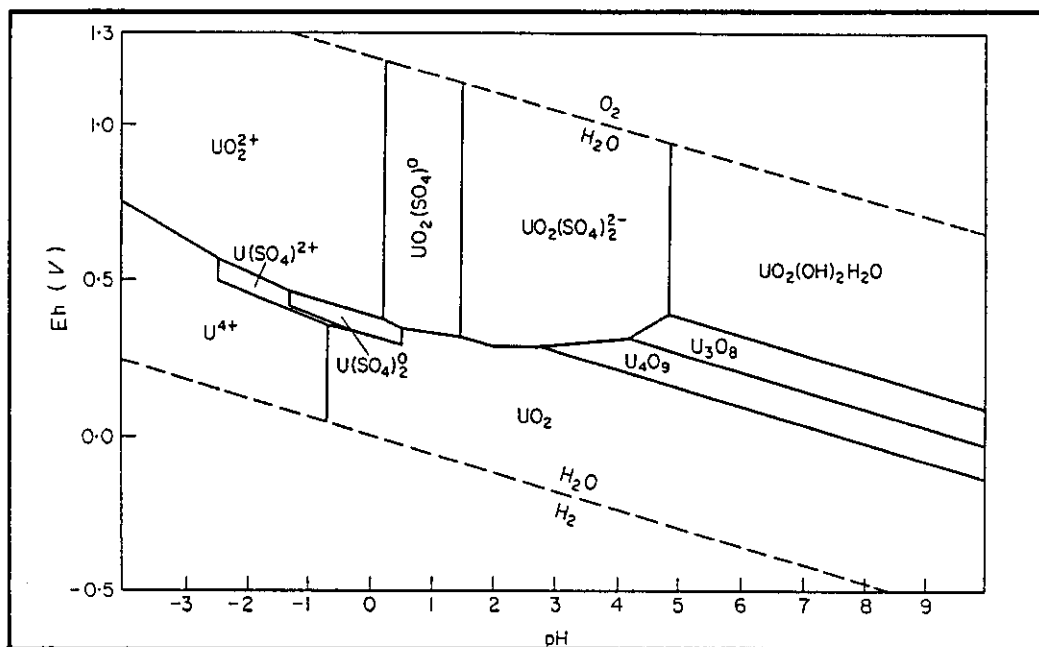


Figure 2, E_h -pH diagram for U-S-H₂O at 25°C.

Activities of U-containing ions = 10^{-2} ; of S-containing ions = 10^{-1} , (after Burkin⁽¹⁾).

In the presence of significant concentrations of sulphate ions, the complex uranium-oxyanion species are much more thermodynamically stable than the simple UO_2^{2+} ion so that the regions of stability of the oxides are much smaller than in the absence of sulphate⁽¹⁾.

Thermodynamic data for brannerite are not available so a Pourbaix Diagram, similar to that for U-H₂O but containing the Ti species and UTi_2O_6 , cannot be constructed. The exhibited refractory nature of brannerite would suggest that the region of stability of the solid is more extensive than that of UO_2 and so more acidic and oxidising conditions would be necessary for any dissolution process. However, the kinetic factors of any process cannot be overlooked. The E_h -pH diagram is based on thermodynamic data only and so gives no

indication of kinetics. In hydrometallurgical processes, kinetics are generally more important than thermodynamic considerations and so the slow kinetics of refractory brannerite dissolution, in comparison to UO_2 , are probably more important factors for investigation than thermodynamic predictions.

1.2.3. Leaching Models

No fundamental leaching study would be complete without a mention of leaching models. References (18), (19), (20) detail many leaching models, but in all cases their applicability to practical leaching is very limited due to the number of assumptions associated with their derivations. Thus, for example, symmetrical particles of uniform size, constant solution concentrations, idealised agitation, etc. are generally assumed. However, despite these reservations, three leaching models were looked at during the course of the present work. It was considered unlikely that, due to the extremely refractory nature of brannerite, any of the models could be fitted exactly, but any correlation at all might give an indication of the mechanisms involved in dissolving the complex mineral.

The three models investigated were:

- (a) shrinking-core for which the kinetics are controlled by diffusion, and dissolution occurs by a uniform removal from a symmetrically-shaped particle. Mathematically, the model can be expressed as:

$$1 - (1 - \alpha)^{\frac{1}{3}} = kt$$

where α = fraction of mineral dissolved

k = constant

t = time.

- (b) shrinking-core, but with a product layer formed on the particle and through which reactants must diffuse inwards to the unreacted core and soluble products outwards from the core. Mathematically:

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = k't, \quad k' = \text{constant.}$$

(A model for the product layer also shrinking is obtained by simple addition of the two expressions).

- (c) a mixed kinetics model for which more than one rate process is involved in the observed kinetics. A model for mixed surface chemical control and diffusion through a product layer can be represented by:

$$\frac{t-t_0}{\Delta n} = \frac{\Delta n}{k''} + k'''$$

where $k'', k''' = \text{constants}$

Δn = number of moles dissolved at time t

$t-t_0$ = time of leaching.

The model typically represents the sum of parabolic and linear rates - the slope contains the parabolic rate and the intercept, the linear rate constant.

No attempt is made here to derive the various models and an interested reader should refer to reference(18).

1.2.4. Uranium Mineral Leaching - Brannerite

Literature on the leaching of any mineral broadly falls into two categories, namely leaching studies on particular ore deposits and fundamental testing of pure (often synthetic) minerals. A literature search of uranium mineral leaching showed that previous investigations obeyed this general rule. However, the chemical nature of

uranium, particularly its polyvalence and the relatively high solubility of the hexavalent form, leads to the existence of many minerals which often show a wide variation of chemical composition within each group. A recent review by Burkin⁽¹⁾ outlines the many proposed modes of occurrence of uranium leading to the wide ore mineralogy. This fact, in conjunction with the exceedingly low concentration of uranium minerals in natural deposits, makes natural ore leaching studies really only applicable to a particular deposit. Not only will leaching characteristics be controlled by the uranium mineral composition, but the chemical nature of the majority gangue will have marked effects. Further, uranium deposits rarely consist of a single mineral, usually several other minerals are closely associated and leaching studies will reflect the nature of the combination. Isolation of the behaviour of a single mineral is virtually impossible. Fundamental studies are again hindered by the wide variation in chemical composition, and the only uranium mineral which has been investigated in any depth is pure UO_2 .

Natural brannerite is no exception to the above observations, but the problem is compounded by two additional factors. Firstly brannerite, because it is a complex multiple oxide, is extremely refractory and therefore difficult to attack chemically under any circumstances. Secondly, the mineral itself undergoes a weathering process by oxidation, producing varying degrees of altered brannerite within a single deposit. These altered brannerites have varying leachability and Clegg and Foley⁽³⁾ reported unweathered brannerite to be exceedingly refractory, with refractoriness increased by the presence of tantalum and niobium but decreased by increasing Ti, Fe and U content. An increasing degree of alteration appeared to improve leachability. Thus it can be concluded that the reported results of brannerite leaching studies are unique to a particular ore deposit

and correlation between the various data is difficult in view of the many unknowns within each system.

George⁽²¹⁾ reported leaching tests on an impure brannerite concentrate from Climax, Colorado. The results showed that only 13% of the uranium was extracted by leaching for 64 hours at ambient temperature with 10% H_2SO_4 . Boiling in 40% H_2SO_4 and HNO_3 yielded extractions of 25-50%. Almost 97% of the uranium was extracted by fuming the concentrate with 1 gramme of 93% H_2SO_4 per gramme of concentrate and digesting the sulphated residue with water. The mineral was reported to be highly refractory.

A Blind River deposit, reported by Clegg and Foley⁽³⁾ as altered grains, was difficultly soluble and high uranium extractions necessitated fine grinding followed by leaching for 48 hours at 50°C in a solution containing about 50 grammes of free H_2SO_4 per litre.

At Stanrock Uranium Mines Ltd., northern Elliot Lake district of Canada, brannerite and thucholite (uraninite combined with hydrocarbons) were treated by leaching for 60 hours at 77% solids at a temperature of $65-70^\circ\text{C}$ with 50 g/l free H_2SO_4 and sodium chlorate used for oxidation. No uranium extraction figures were given⁽²⁾.

Recent reports on current leaching and recovery of uranium in the Elliot Lake region of Ontario have been published by Rio Algom and Denison Mines Ltd.^{(22), (23)}. In both areas, brannerite is one of the minerals of metallurgical significance.

Rio Algom, reviewing the Quirke Lake Mine, report that good leaching of the refractory brannerite material, which predominates in the ore, requires high temperature ($70-75^\circ\text{C}$), long residence time (48 hours but may be

36-40 hours depending on the ore), an oxidant (the air jets in the pachucas are suitable) and a high terminal free acid concentration (typically 50-60 g/l). The ore contains 2.49 lb U_3O_8 per ton and the acid quantity is 90-100 lb, 93% H_2SO_4 per ton of ore. The mesh size of operation is 48% - 200 mesh, 18% + 65 mesh. About 100 mesh appears to be a suitable size. However, a coarser grind can be tolerated because the coarse ground ore fraction (+100 mesh) is lower grade and extraction of 90% plus can still be obtained up to a 28 mesh grind size. Overall, leaching extractions range from 96.5-97% U^{(22), (24), (25)}.

LaRocque and Pakkala⁽²³⁾ have reviewed the operations at Denison Mines. The principal uranium minerals in the ore are brannerite, uraninite and monazite whilst the gangue is mainly silica (>75%), pyrite-pyrrhotite and varying amounts of quartz, chlorite, sericite and rutile. Parallel lines of pachucas are used for leaching and agitation is achieved by air injection. The Elliot Lake ores require high acid concentration, high temperature, (both unlike many of the North American leach plants) and oxidising conditions to effect high extractions. Retention time in the leach plant is usually 36 to 48 hours.

The optimum leaching conditions are influenced by:

- a) the ratio of brannerite to uraninite and monazite. The order of refractoriness is monazite (very high), brannerite and uraninite; brannerite and monazite require high acid concentrations and high temperature but uraninite can be leached at low acid levels under oxidising conditions. The entire ore is treated so that these conditions exist,
- b) the nature of the gangue, particularly the presence of bases which cause high acid consumptions and settling and filtering problems,

- c) the pyrite:pyrrhotite ratio - the pyrrhotite content determines the amount of oxidant (if any) that should be added.

The following parameters are controlled in the leach plant to effect uranium extraction:

- a) acid concentration - a free acid level of 60 g/l is necessary but this has been progressively increased to 75 g/l as it has become more economical to use more acid to reduce the concentration of uranium in the solid tail (0.16 lb/ton down to 0.08 lb/ton);
- b) temperature of 75°C, although a higher temperature would effect higher extractions, the corrosion problem (of rubber pachuca linings) inhibits its use. It has been shown that acid and heat should be added as quickly as possible to the leach circuit.
- c) Oxidation-reduction potential - as much air as possible is injected at the head end of the circuit to oxidise any reducing minerals, after which oxidant, if any, is added. The E_H value is controlled by air injection or 15% sodium chlorate solution additions. Typically the operating potential is 350-450 mV (versus S.C.E.). It is believed that the oxidation of uranium from U^{4+} to U^{6+} proceeds through the ferric-ferrous couple and the air or chlorate acts on the iron in solution^{(22), (24)}.

Fundamental leaching studies on uranium minerals have been almost exclusively confined to UO_2 and references are numerous. Nicol, Needes and Finkelstein⁽²⁶⁾ have reviewed the more important references briefly in their paper and proposed an electrochemical model for the leaching of UO_2 . It is now generally accepted that the electrochemical reaction is one in which the oxidation

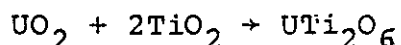
of U(IV) takes place prior to the dissolution stage. The effects of chemical and physical variables on the leaching of UO_2 in acid media have been described in terms of electrochemical considerations and a mathematical relationship developed between rates of leaching of UO_2 and the thermodynamic and kinetic properties of the systems involved.

However, the relevance of a comparison of fundamental leaching of UO_2 to that of UTi_2O_6 is considered limited in view of the particularly refractory nature of brannerite. The crystal structures and strengths of bonding are totally different in the two minerals. The principal common link is that leaching of both oxides requires a reaction that involves the oxidation of U(IV) to the hexavalent state. It is therefore deemed not worthwhile to pursue these studies to any greater depth here and an interested reader should refer to original texts.

Fundamental studies on uranium minerals might have been a more useful source of information for this project, but no work has been done, to the author's knowledge, on the fundamental leaching of any refractory uranium minerals.

1.3. SYNTHESIS OF BRANNERITE

Clearly samples of natural brannerite obtained from the various ore bodies around the world show some degree of variation in chemical composition from the idealised formula of UTi_2O_6 and it might reasonably be expected that each ore body has a unique chemical make-up. Indeed, brannerite mineral particles within a single deposit are likely to show some variation in composition due to the presence of parent rock during formation. It is well known that impurity elements, even down to trace levels, often have an effect on the leaching characteristics of a mineral. Thus, the use of a natural brannerite mineral or minerals for a fundamental study of this nature would have left many questions unanswered as to the effect of each individual impurity. Obviously, what was needed, for a study of this nature, was a "pure" brannerite from which fundamental data could be obtained, and to which controlled "impurities" could be added to monitor their effects. To this end, a method was sought by which brannerite could be synthesised, in sufficient quantities for leaching studies, in a reproducible manner. The most simple chemical reaction that can be written for the formation of brannerite from component oxides is



and it was along this route that the attempt at synthesis was made.

The melting points of UO_2 and TiO_2 are relatively high ($\sim 2900^\circ\text{C}$ and 1825°C respectively⁽²⁷⁾) so a solid/liquid or liquid/liquid reaction of the oxides would have experimental difficulties. A solid/solid reaction appeared to be the most favourable route, but this first

required intimate mixing of the component oxides. The most widely used method of achieving this condition is by fine grinding of the oxides, thorough mixing and subsequent sintering for consolidation and reaction.

To date, no complete phase diagram has been described for the uranium dioxide - titanium dioxide system, but Arthur and Scott⁽²⁸⁾ proposed a simple eutectic type with a eutectic point at 1645°C and approximately 52 W/o "TiO_{1.57}". The "TiO_{1.57}" composition arose due to reduction of TiO₂ by the hydrogen atmosphere in which the measurements were made. Figure 3 shows the Arthur and Scott phase diagram.

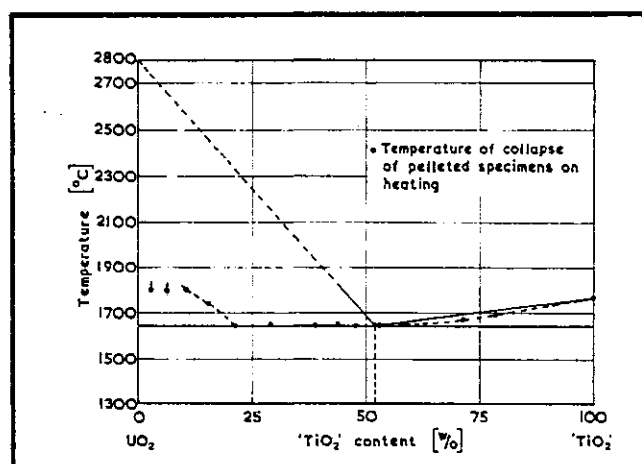


Figure 3, The UO₂-TiO₂ System.

TiO₂ ~ TiO_{1.57} (after Arthur and Scott⁽²⁸⁾).

Ainscough et al.⁽²⁹⁾ corrected these values to 1600-1620°C for a pure UO₂-TiO₂ system. Tresvyatskii and Kushakovskii⁽³⁰⁾ reported that a 50% wt/wt mixture of (UO₂ + TiO₂) heated in air showed a melting point of 1480° ± 30°C.

Gmelin⁽³¹⁾ has provided the most complete review of the UO_2 - TiO_2 system in which the data are presented as compounds of UO_2 with elements of sub-group IV of the periodic table. Hence, all the results are in the form, "The effects of $\text{Ti}(\text{TiO}_2)$ additions to UO_2 ". Much of the information centres on sintering mechanisms and characteristics of $(\text{UO}_2 + \text{TiO}_2)$ mixtures as this seems to be the prime method of combining UO_2 and TiO_2 . Melting of the components does not appear to be a popular route.

A standard sintering procedure for UO_2 has been adopted in nearly all the work on UO_2 and Johnson and Sowman⁽³²⁾ relate the necessary details. Principally, it is a typical ceramic method involving mixing of the starting components, followed by forming (mainly by cold pressing) and sintering in the necessary gas atmospheres at appropriate temperatures.

Uranium dioxide powder will, of course, sinter in the absence of TiO_2 under the appropriate conditions of compaction, temperature and atmosphere by solid state diffusion but the presence of TiO_2 offers a means by which the kinetics of the sintering reaction might be altered. In the absence of a liquid phase, several mechanisms, e.g. volume diffusion, surface diffusion, plastic flow, evaporation-condensation, etc., have been postulated for the transport of material during sintering⁽²⁸⁾. According to theories based on a volume diffusion mechanism, the rate of sintering of UO_2 would be increased by an increase in the rate of diffusion of the slow-moving uranium ion. Experimental evidence does indicate that the presence of TiO_2 does increase sintering rates.

A mechanism for the increase in kinetics of the sintering process of UO_2 , caused by the presence of TiO_2 , has been proposed by Watson and Wilder⁽³³⁾ and Arthur and Scott⁽²⁸⁾. It appeared that in the early stages of sintering,

TiO_2 acted as an oxygen source and consolidation of the sinter was significantly promoted by the diffusion of non-stoichiometric oxygen. At the high temperatures of operation ($1700-1800^\circ\text{C}$), a ductile solid solution was formed that aided sintering and grain growth by straining the lattice near the grain surfaces. This permitted the diffusion of stoichiometric UO_2 at the grain boundaries and some solution of Ti ions in the surface layers of the UO_2 particles. Experimental evidence for this mechanism was based on microstructural analysis of the sinter body which showed rounded grains with a second, intergranular phase which was assumed to be Ti-rich. It has also been generally suggested that a liquid phase formed during sintering which was Ti-rich and which led to the intergranular phase. However, Watson and Wilder⁽³³⁾ and Arthur and Scott⁽²⁸⁾ discounted this possibility except at very high sintering temperatures, although an adequate explanation could not be given and it was indicated that additional work was necessary to clarify the mechanism by which TiO_2 acted as a sinter aid.

Experimental evidence for the increase in sintering rates and, in addition, some improvement in sinter quality by incorporating TiO_2 into UO_2 has been reported as a set of empirical data. However, no adequate explanations or theories have been put forward to account for all the observations, but the mechanism described above seems to be the most comprehensive. The experimental results obtained for UO_2 - TiO_2 sintering can be summarised as:-

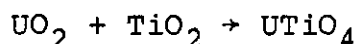
- all the data obtained have been for very small additions of TiO_2 to UO_2 , typically <5%. Even additions $\leq 0.1\%$ strongly affected the ceramic behaviour of UO_2 .
- sintering was usually carried out under a hydrogen atmosphere.
- additions of 0.1-0.5% TiO_2 to UO_2 lowered the required sintering temperature by several hundred degrees, the optimum having been 0.1% TiO_2 ⁽²⁸⁾.

- additions of TiO_2 in amounts 0.1-1.0% were favourable in increasing the sinter density of UO_2 ^{(29), (34), (35)}.
- small amounts of TiO_2 were soluble in UO_2 ⁽³⁵⁾, typically 0.07-0.13% within a grain and 0.24-0.27% at grain boundaries at 1650°C under hydrogen ⁽²⁹⁾.
- it was possible that TiO_2 affected the order of UO_2 , the favoured mechanism having been reduction of TiO_2 and interstitial solution of small Ti ions coinciding with the increased diffusion rate of the slow-moving U ion ⁽³⁵⁾.
- grain growth of a sinter was proportional to the addition of TiO_2 up to the solubility limit. At additions above the solubility limit, the grain growth rate remained constant depending on temperature only ⁽²⁹⁾.
- TiO_2 was not as effective as lower oxides of Ti in promoting grain growth and densification, but was more soluble ⁽²⁹⁾.
- for a combination of very high temperature and TiO_2 additions greater than the solubility limit, a liquid eutectic formed. The eutectic liquid solidified in the range 1600-1620°C. If further sintering was then carried out at (i) $T < 1600^\circ\text{C}$, grain growth was inhibited by the presence of eutectic, or (ii) $T > 1600^\circ\text{C}$, grain growth was enhanced by the liquid eutectic ⁽²⁹⁾.
- the eutectic phase was metastable and a solid/solid transformation occurred during prolonged annealing at 1300°C-1500°C ⁽²⁹⁾.
- in addition to TiO_2 , the following additions to UO_2 showed similar effects: Al_2O_3 , CaO , Cr_2O_3 , MnO_2 , V_2O_5 , Fe_2O_3 , SiO_2 , Nb_2O_5 , ZrO_2 and Cd and B, but to a lesser extent ^{(28), (29)}.
- NiO , Ga_2O_3 , Y_2O_3 , Na_2O_3 and CeO_2 inhibited sintering of UO_2 ⁽²⁸⁾.

- the thermal conductivity of UO_2 was reduced by the presence of TiO_2 ⁽³⁶⁾.
- the oxidation of UO_2 via U_3O_7 to U_3O_8 was only slightly affected by the addition of TiO_2 and the activation energy for this process was practically unaltered ⁽³⁷⁾.

Clearly brannerite/ UTi_2O_6 sintering requires greater TiO_2 additions to UO_2 prior to reaction than have been investigated to date, but the above work is of interest. Early references to brannerite synthesis chose a pyro-synthesis route to reaction, using solid state diffusion to produce a sinter, rather than by melting. The sequence of events in synthesis might be summarised: mixing of U and Ti oxides $\rightarrow$ compaction $\rightarrow$ consolidation/sintering $\rightarrow$ diffusion paths $\rightarrow$ uniform composition $\rightarrow$ reaction to the ternary oxide.

Literature sources point to consolidation of the powder oxides by solid state diffusion rather than by direct reaction to form a ternary oxide. Considering two particles of oxide in contact, the direct reaction, achievable by diffusion would be



Gmelin ⁽³¹⁾ reported that the occurrence of this ternary compound had been mentioned by Darshne and Deshpande ⁽³⁸⁾. It was supposed to have the rhombic YNbO_4 crystal structure, but doubt has been cast on its existence. The compound still requires clear verification.

All the evidence points to sintering having occurred by a solid state diffusion process in which consolidation was achieved by the diffusion of UO_2 and TiO_2 to give, ultimately, a uniform chemical composition whilst still

retaining the original TiO_2/UO_2 crystal lattices. Formation of a new compound, the ternary oxide, followed by the re-ordering of the old lattices to form a new crystal structure.

Of the possible ternary oxides in the $\text{UO}_2\text{-TiO}_2$ system, only UTi_2O_6 with U(IV) and Ti(IV) and UTiO_5 with U(VI) and Ti(IV) have been obtained by solid state reactions between U and Ti oxides and positively identified⁽³¹⁾. Both ternary oxides have been produced by transformation of stoichiometric mixtures of $(\text{UO}_2 + \text{TiO}_2)$ and $(\text{U}_3\text{O}_8 + \text{TiO}_2)$. However, in the case of $(\text{U}_3\text{O}_8 + \text{TiO}_2)$, the order of reaction was the reduction of U_3O_8 to UO_2 followed by the ternary reaction⁽³⁹⁾.

Other oxides such as UTiO_4 , UTi_3O_8 , etc, have been proposed, but none have been reliably confirmed.

Several references (12), (40), (41), (42), (43), (44), have reported the formation of UTi_2O_6 from the oxides of U and Ti by a simple pyrosynthesis route. It was also noted that the uranium mineral brannerite had exactly the same crystal structure and chemical form as the synthesised ternary oxide and it was this connection that gave rise to renewed interest in UTi_2O_6 (brannerite) synthesis.

Although brannerite had been isolated by Hess and Wells⁽⁶⁾ as early as 1920 as being one of the uranium minerals in Stanley Basin, Idaho, and it was generally believed to be one of the uranium-bearing minerals in the conglomerates of the Blind River area of Ontario, the mineral was of a metamict and fine-grained nature. This had rendered identification difficult and analysis was based mainly on X-ray diffraction patterns of heat-treated material. This almost invariably showed the

presence of rutile and anatase, and other minerals closely associated with brannerite. The appearance of the grains was also affected by these impurities. The variable chemical constitution and physical properties of the grains of brannerite had led some geologists to be sceptical about its existence. They put forward the theory that, under the ignition conditions employed to recrystallise the metamict mineral, structural or chemical changes may have taken place which resulted in a compound with the structure of brannerite being formed artificially from a uranium-titanium mineral in the ore or from a mixture of U and Ti oxide minerals.

Kaiman⁽⁴³⁾ undertook the task to determine whether a compound with the structure of brannerite could be synthesised from oxides of uranium and titanium under the usual ignition conditions. The typical procedure involved grinding together weighed amounts of oxide reagent in an agate mortar to ensure thorough mixing. The charges were heated under controlled atmosphere and temperature conditions in a high frequency furnace, Pt/Rh resistance furnace or in a Meker burner. The heated charges were cooled slowly to ambient temperature and the crystalline phases in the products were determined by X-ray diffraction analysis.

Charges: $\text{UO}_2 + \text{TiO}_2$, $\text{UO}_2 + \text{U}_3\text{O}_8 + \text{TiO}_2$, $\text{TiO}_2 + \text{UO}_3$

Temperature: 1000°C

Controlled atmosphere: air, vacuum, O_2 -free argon

Result: there was no interaction between the oxides indicating that a synthetic compound could not be formed from U-Ti minerals under standard ignition conditions.

Conclusion: brannerite occurred as a mineral in nature.

Subsequent tests showed that brannerite could be formed by ignition but only at significantly higher temperatures in the presence of calcium compounds which acted as a flux and catalysed the reaction.

On proving the ignition route to be unsuccessful, Kaiman carried out further tests to determine the conditions necessary for brannerite synthesis and thereby establish the ideal composition of brannerite. Experiments were carried out by heating charges consisting of U-Ti oxides in argon:

Charge: (UO_2 , U_3O_8 , UO_3) + TiO_2 , the molar proportions were $\text{UO}_2:\text{TiO}_2 = 1:2$ and $1:2.5$

Atmosphere: O_2 -free argon

Temperature: 1400°C

Time: 90 minutes

Results: (i) $\text{UO}_2:\text{TiO}_2 = 1:2$

- a sintered product which contained a brannerite phase as the major constituent.
- microscopical analysis showed the phase to be homogenous except for trace amounts of unreacted oxides.
- X-ray powder pattern analysis showed that the compound was iso-structural with heat-treated brannerite. The two materials had very similar unit cells; minor differences in the position and intensity of the diffraction lines were accounted for by the presence of Ca, Th, rare earth, Pb and other ions substituting for U in the structure of the natural minerals.

(ii) $\text{UO}_2:\text{TiO}_2 = 1:2.5$

- a sintered product containing brannerite as a major phase with a second phase (TiO_2) present. The sintered brannerite could not be produced when the charges were treated in air.

Conclusion: a homogenous, sintered compound, iso-structural with the complex oxide mineral brannerite, could be pyrosynthesised under the conditions above.

Running concurrently with the work of Kaiman was a research programme of Patchett and Nuffield⁽¹²⁾. They too showed that brannerite was a constituent of an ore and not a result of synthesis from oxides under oxidising ignition conditions. The ignition conditions employed were similar to those of Kaiman in that mixtures of pitchblende and rutile (or anatase) in the ratio 2:1 were heated in an open crucible. The mixture recrystallised to U_3O_8 and rutile. The same result was obtained when the mixture was seeded with natural brannerite from Blind River. Further, an excess of carbon added to the crucible to prevent the formation of U_3O_8 gave an ignition product of UO_2 and rutile.

In an attempt to synthesise brannerite, Patchett and Nuffield added sodium chloride to the above mixture. The flux reacted with the mixture to produce a compound, possibly a sodium uranium oxide, whose diffraction data showed some similarity to those of brannerite.

A similar reaction was reported by Schröcke⁽⁴¹⁾ who identified the compound formed as $Na_2U_2O_7$. Further work showed that a sinter of UO_2 - TiO_2 could be made by heating $1 UO_2 + 2 TiO_2$ under vacuum at $1000^{\circ}C$. On adding this sinter to a NaCl-melt under vacuum and maintaining a temperature of $1000^{\circ}C$ for 24 hours, shiny black crystals formed without any side reaction. These crystals were identified as UTi_2O_6 .

Öztunali⁽⁴⁰⁾ showed that brannerite could be made by incorporating a stoichiometric mix of $1 UO_2 + 2 TiO_2$ into a (NaCl + KCl) salt melt. The conditions of synthesis were $1000^{\circ}C$, under vacuum for 50 hours.

Clearly a chloride salt melt provides a route to brannerite synthesis, but the presence of sodium or (sodium + potassium) ions and the possible entrainment of melt prohibit the synthesis of a pure UTi_2O_6 compound.

Patchett and Nuffield extended their original work to synthesise pure brannerite. A procedure of two-stage sintering followed by melting was the result:-

- (i) Charge: very pure tetravalent uranium oxide + reagent grade TiO_2 in the atomic proportions of 1:2. The powders were finely ground and pressed into a pellet.

Conditions: sintered at low vacuum (10^{-3} mm Hg) in a graphite crucible for 18 hours at 900°C .

Result: no chemical change but sinter formed.

- (ii) Charge: sinter from above, reground.

Conditions: 1200°C under the same conditions of vacuum, crucible and time as above.

Result: a sinter product which gave a composition X-ray pattern of UO_2 and brannerite.

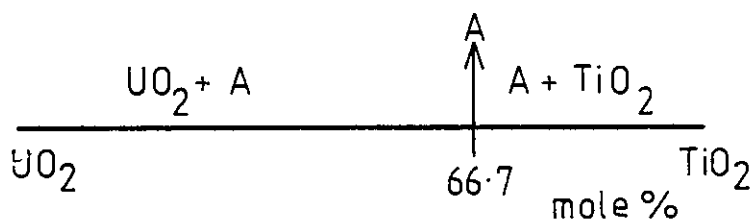
- (iii) Charge: sinter pellet from (ii)

Conditions: the pellet was melted in an arc furnace under a low pressure of argon. An adjustable electrode was used to break the arc over the pellet to produce large currents sufficient to easily melt the sinter. The estimated pellet temperature on arcing was 2000°C . A water-cooled base ensured rapid cooling of the pellet.

Result: the portion of the pellet which had rested on the base still contained a slight area of UO_2 , but the remainder was composed entirely of brannerite. The X-ray data of synthetic and ignited brannerite were in excellent agreement.

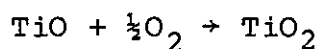
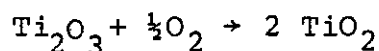
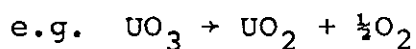
Conclusion: Patchett and Nuffield had produced a quick and reproducible method of preparing pure brannerite by a combination of sintering and melting the component oxides.

Bobo⁽⁴⁴⁾ made a brief reference to the synthesis of UTi_2O_6 in which it was reported that stoichiometric mixes of uranium and titanium oxides held under vacuum (10^{-3} mm Hg) at 1000°C for 15 hours produced an incomplete reaction. However, on raising the temperature to 1400°C , a pure UTi_2O_6 phase was formed after 3 hours' sintering. Non-stoichiometric mixes were also treated to produce a schematic composition diagram:

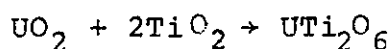


where A is the unique phase UTi_2O_6 .

Bobo further reported that UTi_2O_6 was only synthesised from UO_2 and TiO_2 . Synthesis from lower oxides of Ti with higher oxides of U was preceded by a series of oxidation/reduction reactions



followed by



Radzewitz⁽⁴⁵⁾ carried out a similar synthesis in the ThO_2 - TiO_2 system and reported the formation of ThTi_2O_6 , with two allotropic modifications, synthesised at 1000°C and 1400°C . The higher temperature form, β - ThTi_2O_6 , was identified as having the monoclinic crystal structure.

No work, known to the author, has been published to date on the synthesis of brannerite with controlled amounts of impurity, the so-called doped brannerite. Doping of the mineral is considered to be the next important step in that replacement of uranium and titanium in the lattice by other elements imitates more closely the naturally-occurring mineral. This system should give more realistic results in, for example, leaching studies.

1.4. CRYSTALLOGRAPHY AND DIFFRACTION PATTERNS OF BRANNERITE

Leaching characteristics are affected by many factors, one of which is often the crystal structure of the mineral under consideration. The leachability of a mineral could be determined by, for example, crystal type, close-packing, bond lengths and strengths, accessibility and availability of metal ions, diffusion paths, degree of disorder, impurities, etc., and hence a knowledge of the structural nature may give an indication of the mechanism of dissolution.

Impurity ions in the lattice may either substitute into the parent structure or lie in interstitial sites. In either position they will inevitably distort the ordered lattice. In an interstitial site, an impurity ion will inhibit normal ion movement in the parent lattice. Substitutional impurities could affect leachability in a number of ways:-

- differing ionic radii leading to distortion of the lattice,
- differing valencies producing vacancies in the metal or oxygen substructure to maintain charge neutrality. This often leads to enhanced diffusion paths,
- chemical affinity between parent and impurity,
- altering electrical conductivity due to the electron defect configuration, a semi-conductor effect,
- impurities present may also be preferentially soluble during leaching leaving behind a crystallographically "porous" structure, hence enhancing subsequent diffusion and leaching.

In the current exercise, brannerite was synthesised to model leaching characteristics. In such a fundamental study it was important that the synthetic mineral was

iso-structural with naturally occurring deposits. However, the determination of the exact crystal structure was not a primary target of this project, so only a brief literature review is given and further details can be obtained from the original texts referenced.

As has already been discussed, natural brannerite is found in a metamict form - it has the properties of an amorphous solid, but retains the original external crystalline form. Thus, for example, reported X-ray data are nearly always for brannerite which has been reheated to reproduce the original crystal structure.

In the original work on brannerite, Hess and Wells⁽⁶⁾ reported that natural brannerite crystal grains from Stanley Basin seemed to have a prismatic tendency and were believed to be orthorhombic or tetragonal from this external appearance. Work by Larsen, reported by Hess, showed the mineral to be isotropic and Hess concluded that it was probably an isometric paramorph of either a tetragonal or orthorhombic form, as many of the complex pegmatitic uranium minerals seemed to be. Acicular (needle-shaped) crystals were also described. Pabst⁽⁴⁶⁾ obtained readings from brannerite crystals from California on a reflecting goniometer. He found that the angles were close to those of a tetragonal zone, but the development was orthogonal. A single orthogonal zone dominating the habit is to be expected only in orthorhombic or monoclinic crystals.

Schröcke⁽⁴¹⁾ proposed the columbite structure for UTi_2O_6 with:-

$a = 6.18, \quad b = 14.24, \quad c = 5.73 \text{ \AA}$
 of columbite $a = 5.74, \quad b = 14.27, \quad c = 5.09 \text{ \AA},$

the corresponding crystal planes being (002), (041) and (111).

However, more up-to-date literature generally regards brannerite as being monoclinic or triclinic, although the data vary somewhat. The triclinic model was proposed due to the morphology of synthetic brannerite and the very coarse crystals of some pegmatites. For this reason Öztunali⁽⁴⁰⁾ described a triclinic unit cell with

$$\begin{aligned} a_0 &= 5.27, \quad b_0 = 3.54, \quad c_0 = 6.31 \text{ \AA} \\ \alpha &= 77^\circ 30', \quad \beta = 108^\circ 10', \quad \gamma = 100^\circ 10' \quad (\text{all } \pm 1^\circ) \\ &\text{one molecule per unit cell i.e. } Z = 1, \quad V = 118.4 \text{ \AA}^3 \end{aligned}$$

The data were obtained from a 0.07 mm size crystal using rotating crystal and Weissenberg photographic techniques. (Patchett and Nuffield⁽¹²⁾ have, however, pointed to possible errors in Öztunali's calculations and new calculations indicated that the discrepancy between measured and calculated d-spacings was too great to be eliminated by refining the triclinic element).

Öztunali confirmed the work of Schröcke to a degree by commenting that this system closely resembled the columbite structure, where columbite is a natural iron niobate or tantalate: FeNb_2O_6 , FeTa_2O_6 or $(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6$. It is worth noting, though, that Öztunali and Schröcke performed experiments on brannerite from chloride melts and the columbite resemblance was particular to these systems only.

Patchett and Nuffield⁽¹²⁾ took a monoclinic unit cell based on results obtained using a method similar to that of Öztunali. It was found that the X-ray data could be easily indexed as monoclinic with

$$\begin{aligned} a &= 9.87, \quad b = 3.76, \quad c = 6.95 \text{ \AA} \quad (\text{all } \pm 0.02 \text{ \AA}) \\ \beta &= 119^\circ 30' \quad (\pm 15'), \quad \text{space-group } \frac{C2}{M}, \quad Z = 2 \\ &(\text{i.e. two molecules of } \text{UTi}_2\text{O}_6 \text{ per unit cell}). \end{aligned}$$

Radzewitz⁽⁴⁵⁾ confirmed these values with

$$a = 9.79, \quad b = 3.77, \quad c = 6.91 \text{ \AA}$$

$$\beta = 119.83^\circ$$

George⁽¹⁶⁾ also reported a monoclinic system in which the fracture planes of natural brannerite were (110), (130), (010) and (201).

There appears to be a great deal of confusion in the literature in the choice of either a monoclinic or triclinic system. However, this is not too surprising because in brannerite there is, apparently, a very close correlation between the two. A space model of the brannerite lattice proposed by Ramdohr⁽¹¹⁾ gives the relationship between the two orientations and the indexing directions (Figure 4).

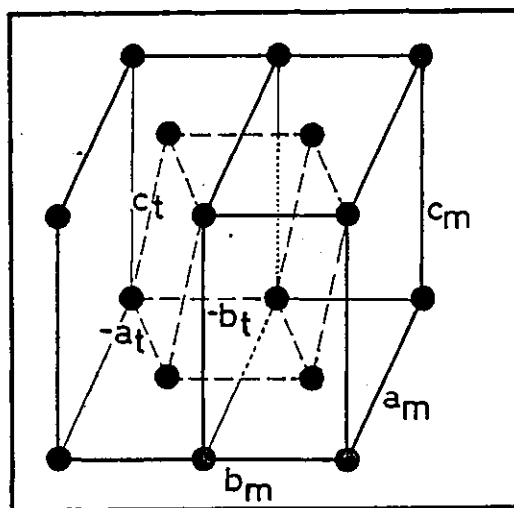


Figure 4 - Relation of the triclinic and monoclinic cell of brannerite

What is clear is that brannerite is nearly always isotropic with $n \approx 2.3$. Typically $n_{Li} = 2.26 \pm 0.02$, $n_{Na} = 2.30 \pm 0.02$ ⁽¹⁶⁾. It was suggested that the mineral

was isotropised by its high content of uranium. This was often connected with a small amount of the alteration process $U^{4+} \rightarrow U^{6+}$. Thus, in the natural mineral, an amount of TiO_2 corresponding with the U^{6+} did not fit into the lattice and was freed, usually to form small quantities of anatase. This was sometimes picked up on X-ray analysis, particularly on metamict brannerite, which showed no (or very few) lines except for this alteration product. This gave an idea of the extent of $U^{4+} \rightarrow U^{6+}$ alteration⁽¹¹⁾.

Zoning was also a possibility in natural brannerite which could have explained variations in the concentration of TiO_2 (anatase) exsolution particles. Twinning was not observed⁽¹¹⁾.

An exhaustive structure analysis for this type of compound exists only for the corresponding thorium mineral $ThTi_2O_6$ ⁽³¹⁾.

X-ray diffraction data are by far the simplest and most widely used method of analysis, identification and confirmation of brannerite. With this method it is possible to trace impurity levels down to typically 3-5%. Important parameters in identification are the highest d-spacing and most intense lines. In the available literature brannerite was generally confirmed by these factors. Many authors^{(12), (40), (41), (44), (46)} have reported diffraction data on heated natural brannerite and synthetic brannerite, all of which were in close agreement in terms of both highest d-spacing and line intensity. The most reported lines were:

highest d-spacing($\text{\AA}$): 6.07, 6.03, 5.88, 6.03, 6.04, 6.06
 most intense lines($\text{\AA}$): 4.77, 4.74, 4.73
 3.42, 3.41, 3.41, 3.43, 3.44, 3.41
 3.32, 3.32, 3.29, 3.27, 3.28) 3.32
 3.35)
 3.37)
 2.455, 2.462, 2.449, 2.46, 2.47, 2.46
 2.276, 2.276, 2.27, 2.281, 2.29, 2.29
 1.903, 1.903, 1.903, 1.903,
 1.861, 1.864, 1.857, 1.866 1.864
 1.623, 1.625, 1.618, 1.621

The slight variations were probably due to impurity elements in natural brannerite.

The A.S.T.M. card index of diffraction patterns lists two forms of UTi_2O_6 as brannerite, numbers 8-2 and 12-477. Table 2, below, shows these patterns. There is close correlation between the two patterns, the slight variations in d-spacing probably arising due to impurities in the natural deposit. Other patterns in the U-Ti-O system which are necessary for confirmation of brannerite, either natural or synthetic, are too numerous to reproduce here, but are obtainable from standard A.S.T.M. literature.

Much work has been done on correlating d-spacings with the various models to identify crystal planes and angles. This has included work on synthetic, natural and ignited brannerites. However, most of this work is speculative, based on the "best-fit" planes of the crystal structure proposed by individual authors, and there is very little correlation between the various texts. It is not considered worthwhile reproducing the many and varied speculative proposals here; interested readers should refer to the original papers of Patchett and Nuffield⁽¹²⁾, Pabst⁽⁴⁶⁾, Schröcke⁽⁴¹⁾, Bobo⁽⁴⁴⁾ and Ramdohr^{(10), (11)}.

8-2 MAJOR CORRECTION

d	3.42	1.90	2.46	6.07	UT ₁₂ O ₆				
1/λ _i	100	80	70	30	URANIUM TITANIUM OXIDE BRANNERITE				
Rad.	λ	Filter	Dis.	d Å	1/λ _i	hkl	d Å	1/λ _i	hkl
Cut off	1/λ _i			6.07	30	001	1.700	40	
Ref. PAST, AM. MIN. 39	109 (1954)			4.70	50	201	1.623	60	
				4.31	20	200	1.609	40	
				3.42	100	110	1.585	20	
				3.32	80	202	1.569	50	
Sys. MONOCLINIC			S.G. C ₂ /m (12)	3.02	30	002	1.557	30	
a 3.79	b 3.72	c 6.27	A 2.63 C 1.85	2.91	50	201	1.489	10	
α 118°25'	γ	β	Z 2 Dx 6.486	2.76	40	111	1.481	20	
Ref. LGB BY ANALOGY WITH SYNTHETIC UT ₁₂ O ₆				2.511	40	112	1.461	13	
				2.455	70	311	1.440	25	
Fe	n _{Fe}	mp	fy	2.426	20	401	1.411	8	
2V	D		Color	2.276	70	310	1.371	45	
Ref.				2.151	20	400	1.308	25	
				2.080	10	112	1.289	14	
				2.029	40		1.268	18	
				2.017	20		1.255	30	
				1.903	90		1.242	8	
				1.861	60		1.230	30	PLUS ABOUT
				1.776	10		20 MORE LINES, MOSTLY		
				1.729	30		BROAD AND DIFFUSE		

SPECIMEN FROM MONO COUNTY, CALIFORNIA; HEATED TO ABOUT 1000°C.

SIMILAR PATTERNS GIVEN BY HEATED BRANNERITE FROM CUSTER CO., IDAHO AND BOU-AZZER MINE, MOROCCO.

CHEMICAL ANALYSIS: SEE DATA FOR UNHEATED BRANNERITE.

12-477 MAJOR CORRECTION

d	3.44	3.35	4.74	6.04	UT ₁₂ O ₈	(BRANNERITE)					
1/I ₁	>100	>100	95	35	URANIUM TITANIUM OXIDE						
Rad. CuKα	λ 1.5418	Filter Ni	Dia.			d Å	1/I ₁	hkl	d Å	1/I ₁	hkl
Cut off	1/I ₁ DIFFRACTOMETER					6.04	35	001	1.903	20	311
Ref. PATCHETT and NUFFIELD, CAN. MINERAL. 6 483 (1960)						4.74	95	201	1.981	25	020
						4.29	20	200	1.798	4	021
Sys. MONOCLINIC	S.G. C2/c (12)					3.44	>100	110	1.749	8	221
a 9.8016	b 3.7620	c 6.9125	A 2.605	C 1.837		3.35	>100	202	1.732	6	512
β 118°58'	γ	Z 2	Dx 6.398			2.29	14	111	1.723	4	220
Ref. IBID. (FROM A SINGLE CRYSTAL)						3.02	35	002	1.709	20	204
REFINED ON 31 LINES					V 223.08	2.90	35	201	1.675	6	404
2θ	n = β	ψ γ	Color	Sign		2.77	30	111	1.642	8	222
D 6.35	mp					2.53	30	112	1.630	20	513
Ref. IBID.						2.47	30	311	1.609	18	113
						2.41	18	401	1.597	6	022
						2.303	8	203	1.578	10	221
						2.292	25	312	1.569	8	314
						2.276	12	310	1.561	6	510
						2.144	10	400	1.556	6	203
						2.090	4	112	1.493	28	114
						2.043	35	403	1.486	4	421
						2.015	25	003	1.450	4	402
						1.911	6	113	PLUS 12 LINES TO 1.200		
SYNTHETIC PRODUCT, SINTERED UO ₃ +2TiO ₂ AT 900° AND 1200° AND MELTING IN AN ARC AT ABOUT 2000°C. FOR SIMILAR POWDER DATA SEE OZTUNALI, N. JAHNS. MINERAL. MONFASH. 197 (1959).											

What is abundantly clear is that no single crystal structure has, to date, been exactly defined for brannerite, but Patchett and Nuffield seem to be the closest with their agreement between measured and calculated d-spacings for a monoclinic system.

SECTION 2

EXPERIMENTAL PROCEDURE

2.1. X-RAY DIFFRACTION ANALYSIS OF SYNTHETIC BRANNERITES

The principal method of analysis of the minerals synthesised by the procedures described in the next section (and the subsequent leach residues) was X-ray powder diffraction. The camera used was a Guinier de Wolff type using Co K α radiation ($\lambda = 1.7902 \text{ \AA}$), with generator settings of 30 kV and 20 mA and exposure times of 3 hours. The X-rays, which were monochromated and focussed by a curved quartz crystal, were transmitted through the powder specimens and recorded on semi-cylindrical X-ray film.

For rapid analysis, the line positions of the patterns were measured using the Co K α calibrated rule and compared with A.S.T.M. standard patterns.

For accurate measurement of d-spacing, particularly in the case of correlating doping additions to change in lattice spacing, an accurate magnifying vernier was employed. This method was also used to check and monitor any change in crystal structure in leach residues.

The camera was first calibrated using salt and silica standards (which have simple powder patterns) to find the camera constant. The formula connecting the measured d-spacing to the distance of a line from d_{∞} is given by

$$\lambda = 2d \sin kx \quad (1)$$

λ = wavelength of incident radiation (in $\text{\AA}$)

d = d-spacing from standard A.S.T.M. files (in $\text{\AA}$)

k = camera constant

x = distance of line from d_{∞} (in mm) measured by
magnifying vernier
 kx is in degrees

Using the known standards, and hence d-spacings from the A.S.T.M. file, $kx_{(theory)}$ values were calculated from (1). Plotting $kx_{(theory)}$ against $x_{measured}$ for all the lines on the two standard patterns gave a straight line with slope = k , the camera constant. Typically the camera constant was found to be ~ 0.25 degrees/mm. In subsequent analyses of the unknown specimens, x was measured accurately, kx found and hence, an accurate value of d-spacing evaluated.

Identification of a synthetic mineral was made by comparison of d-spacings and relative line intensities with those recorded on the A.S.T.M. files for brannerite, numbers 8-2 and 12-477.

This X-ray method of analysis was chosen for a number of reasons:

- it is quick and accurate,
- it is sensitive and can show up phases with 3-5% of the total. If a phase has a particularly intense line, it is possible to record levels $\sim \frac{1}{4}\%$ of the total,
- there is very little background intensity, allowing very weak lines to be recorded,
- the method of sample preparation is simple and requires a minimal quantity of specimen (although care must be taken to ensure a representative sample). Particulate specimens were ground in an agate mortar to a very fine size and then mounted in the specimen holder backed by sellotape,
- up to four samples can be examined at any one time,
- the camera/pattern is easily calibrated, either by incorporating an internal standard (e.g. NaCl, SiO_2

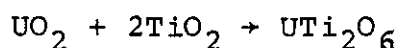
- on one of the tracks or by total external calibration,
- very reproducible results are given, i.e. provided that the radiation is carefully focussed each time of use, the camera constant does not vary significantly.

2.2. SYNTHESIS OF BRANNERITE

The aim of the present work was to produce a pure, synthetic brannerite which was iso-structural with natural brannerite deposits but which did not contain any impurities normally associated with natural brannerite. Thus, a fundamental leaching study could be undertaken and controlled impurities introduced when necessary to investigate their individual effects.

The starting point of experimental work on brannerite synthesis was an attempt to reproduce the methods of the successful authors, outlined in the literature survey. However, no attempt was made to emulate the Patchett and Nuffield⁽¹²⁾ method of synthesis from chloride melts. It was felt that this would have led to contamination of any brannerite produced by substitution in to the lattice, interstitial ions in the lattice or by simple entrainment of the melt. Naturally this would have destroyed the purpose of the synthesis.

Most of the literature available indicates that UTi_2O_6 was formed from a UO_2/TiO_2 system and the use of higher oxides of uranium and lower oxides of titanium involved a first step of reduction/oxidation to UO_2/TiO_2 . Hence, it was decided that a UO_2/TiO_2 mix was the most sensible starting mixture to enable a direct reaction route to be undertaken:



The starting materials were:

- UO_2 supplied by Koch Light Ltd., 99.97% pure, depleted,
- TiO_2 supplied by Laporte Industries Ltd. as Tiona VC, a pigment base. The typical analysis was:

TiO_2	= 99.3%	SnO_2	= 30 ppm
Al_2O_3	= <0.1%	PbO	= 25 ppm
P_2O_5	= 0.07%	V_2O_5	= 20 ppm
SiO_2	= 0.05%	Cr_2O_5	= 5 ppm
SO_4	= 0.02%	As_2O_5	= 2 ppm
K_2O	= <0.01%	$\text{NiO}, \text{CuO}, \text{CeO}_2$	) all <2 ppm
MgO, ZnO both	= 0.002%	$\text{MoO}_3, \text{CdO}, \text{Sb}_2\text{O}_3, \text{B}, \text{F}$	
CaO	= 300 ppm	BaO	= 1 ppm
Nb_2O_5	= 150 ppm	$\text{Se} + \text{Hg} + \text{Bi}$	<2 ppm
$\text{Fe}_2\text{O}_3, \text{WO}_3$ both	= 40 ppm		
ZrO_2	= 35 ppm		

The particle size of this grade was around 10 microns.

Quantities of UO_2 and TiO_2 powders were separately and carefully ground to a fine dust using a pestle and mortar. Care was taken to avoid contamination and inhalation of dust, particularly UO_2 . A stoichiometric mix was made for the synthesis with a mole ratio of $\text{UO}_2:\text{TiO}_2 = 1:2$. Thorough mixing of the two powders was achieved by placing the mixture in a cylindrical drum and rolling it for 24 hours. This was followed by a standard "coning and quartering" technique to produce homogeneous samples for synthesis.

X-ray diffraction patterns were processed for UO_2 , TiO_2 and the stoichiometric mixes for synthesis for use as standards and to check the purity of the starting materials. A full treatment is given in the "Results and Discussion" section.

In the following paragraphs a description of the attempts at brannerite synthesis undertaken is given. Full experimental results and discussion are given in the

"Results and Discussion" section. However, to maintain continuity of experimental logic, very brief details of results are outlined after each synthesis procedure. To avoid repetition in the Results section, a simple statement only as to the success or otherwise of a synthesis route is given.

In view of Kaiman's⁽⁴³⁾ success in producing brannerite by a pyrosynthesis route of holding stoichiometric amounts of $(\text{UO}_2 + \text{TiO}_2)$ in oxygen-free argon, at 1400°C , for 90 minutes, it was decided that a repeat synthesis was to be the first attempt undertaken.

The requirements for the synthesis furnace were considered to be:

- a furnace capable of withstanding a temperature of 1400°C for a sustained period of time,
- a furnace capable of holding a crucible over which O_2 -free argon could be passed at a pressure slightly higher than atmospheric, to maintain an air-free system,
- a crucible made of a material which would not affect the reactants chemically.

The design chosen was a tube furnace as part of an R.F. furnace system. The furnace tube ($2\frac{1}{2}$ " I/D, 3' long) was made of mullite (maximum operating temperature = 1500°C), closed at one end. A water-cooled copper coil was placed over the closed end to act as the inductor, the ends of the coil being attached to an R.F. set for water and power supplies. The mullite tube was supported on firebricks and the hot-zone (coil area) well insulated with fire-blanket material.

The open end of the furnace was sealed with a silicone rubber bung through which three narrow-bore mullite tubes

were introduced into the furnace for the purpose of:

- (i) a gas inlet taking O_2 -free argon directly to the hot-zone from a high purity argon cylinder,
- (ii) a gas outlet attached to a standard bubbler system to monitor the gas flow rate and to ensure a positive argon pressure in the tube, to prevent air leakage into the furnace,
- (iii) holding a mullite-sheathed thermocouple which was placed in the hot-zone to measure precisely the synthesis temperature.

The furnace was arranged horizontally so that a crucible, supported on a piece of fire-blanket, could easily be slid into and removed from the hot-zone. Two cylindrical fire-brick plugs placed between the crucible and the bung reduced heat loss.

A graphite crucible was chosen to fulfil two purposes; firstly, to hold the reactants and second, to act as a susceptor.

Tests carried out in the absence of reactants showed that the furnace was easily capable of sustaining $1400^{\circ}C$, provided that heating and cooling were carried out gradually to avoid cracking the tube. Mullite has poor thermal properties, particularly a low coefficient of expansion. The graphite crucible was heated in the absence of reactants for several hours during these tests to remove any volatile substances.

To repeat Kaiman's successful synthesis, approximately 70 grammes of the stoichiometric ($UO_2 + TiO_2$) mix was packed into the crucible and consolidated by means of a cold press. The crucible was placed in position in the furnace tube and the system flushed with argon for 2 hours, to remove all traces of air, since Kaiman had reported that

the reaction could only take place in an inert atmosphere. Heating was commenced and a temperature of 1400°C held for 90 minutes. The furnace was subsequently cooled (slowly) to ambient temperature, the crucible removed and the product analysed by X-ray diffraction. Oxygen-free argon was passed through the furnace system at a slow rate throughout the whole process of heating, sintering and cooling.

Result: sintering of powder but no chemical reaction.

The second synthesis attempt followed the experimental procedure of above, but the consolidated ($\text{UO}_2 + \text{TiO}_2$) powder was held at 1400°C for 24 hours.

Result: sintering of powder ; a scale product in contact with the graphite crucible; brannerite not present.

The third synthesis approach followed the standard pyrosynthesis route, but the reactants were contained in a re-crystallised alumina boat, lining the graphite crucible, to avoid reduction of the TiO_2 by carbon. Heating was carried out for 1 week at 1400°C .

Result: sintering of powder ; a scale product in contact with the alumina boat; no trace of brannerite.

At this stage, it became clear that a pyrosynthesis route to brannerite, although reportedly feasible, had not proved successful. Indeed, no hopeful signs had been given in that none of the attempted routes had even shown any brannerite, which by X-ray diffraction should have been detected at levels as low as 3-5%. To compound the problem, a great deal of trouble was encountered with cracking of the mullite furnace tubes during the heating/cooling cycles. Not only was this an experimental hindrance, but it was proving to be prohibitively expensive. Thus, a decision was made to abandon a pyrosynthesis route using an R.F.

furnace system. An alternative method of synthesis was sought using an arc-melting furnace to reproduce the work of Patchett and Nuffield⁽¹²⁾.

The arc-melting furnace employed an arc struck between a tungsten electrode and a water-cooled copper hearth. The hearth consisted of several wells to hold various samples. The mode of use was to flush the furnace several times with oxygen-free argon, evacuating between flushings. The furnace was finally evacuated and a small partial pressure of argon introduced to permit striking of the arc. A small button of titanium was always placed in one of the wells. This was melted prior to melting the samples so that it could act as an "oxygen-getter".

The arc furnace was not suitable for melting mixtures of powders so, either the ($\text{UO}_2 + \text{TiO}_2$) mix was cold-pressed into pellets or a short pyrosynthesis was undertaken to produce a sinter. It was shown that the methods gave identical results and both treatments were used, depending on which was more convenient at the time of experiment (e.g. availability of press, furnace, etc.).

Samples of the ($\text{UO}_2 + \text{TiO}_2$) mix, either as a pellet or sinter, were treated in the furnace. Once molten, the samples were held in the liquid state for varying lengths of time to allow thorough mixing and possible reaction. Thorough mixing was observed, due to the action of the arc causing rapid eddying. The samples were allowed to solidify, the pellets flipped over and the whole process repeated to ensure homogeneity. The estimated temperature of the arc was 2300°C .

Several conditions of melting were employed, changing the time of heating, reheating, etc., and to avoid repetition the detailed experimental conditions are given

in the "Results and Discussion" section. In all cases, the solid pellets were crushed and analysed by X-ray diffraction.

General Result: only a trace amount of brannerite was produced in all cases; the majority of all the pellets still consisted of a mixture of UO_2 and TiO_2 . Several unidentified lines on the X-ray films were observed, in all cases, which were assumed to have arisen from contamination by the tungsten electrode or the copper hearth. The intensity of the lines increased on remelting the samples or holding the samples in the molten state for longer periods of time. The possibility of the lines having arisen from a super-structure (caused by quenching) was eliminated by re-analysing the samples after a period of annealing.

Clearly, contamination of any kind defeated the object of the synthesis programme, so melting techniques were abandoned and solid-state routes re-investigated.

In view of the problems encountered in the use of an R.F. furnace, a normal laboratory, high-temperature, horizontal, tube-furnace was employed for a fourth pyrosynthesis, although this drastically reduced the quantity of material that could be treated at any one time. The furnace consisted of a 3' long, open-ended mullite tube with platinum windings wound directly on to the ceramic, along the central 1' length. The hot zone was encased in an insulated box. The temperature controls, with rheostat and back-windings, allowed control of a steady temperature of $1400^{\circ}\text{C} \pm 10^{\circ}\text{C}$. The ends of the tube were tapered and fitted with "Quick-fit" pyrex adaptors, which were sealed with heat-resistant silicone grease. This allowed both easy removal of fittings and an air-tight seal.

Oxygen-free argon gas was passed in from a cylinder at one end of the tube and out via a bubbler from the

other. The mix of ($\text{UO}_2 + \text{TiO}_2$) for synthesis was contained in a re-crystallised alumina boat, in the hot-zone of the furnace. Firebrick plugs were placed in the tube, at either end of the hot-zone, to help reduce heat loss.

A similar procedure to that of the original pyrosynthesis was adopted, but only 35 grammes of the mix could be compacted into the alumina boat. The boat was held at 1400°C , under oxygen-free argon, for 6 weeks and then cooled to ambient temperature over a period of 3 days. The product was removed and samples taken from the surface and positions within the bulk for X-ray diffraction analysis.

Result: a successful synthesis; a porous sinter composed entirely of brannerite.

In order to produce a fully dense sample of brannerite, a portion of the above sinter was vacuum arc melted using the procedure previously outlined. The brannerite was held in the liquid state for a minimum time and the cooled pellet analysed by X-ray diffraction.

Result: the pellet consisted of ($\text{UO}_2 + \text{TiO}_2 + \text{brannerite}$) plus a small quantity of an unidentified phase. Melting had produced a breakdown of the brannerite structure into the constituent oxides.

The abandonment of melting techniques, and the subsequently-proven reproducibility of the pyrosynthesis route, led to a standard procedure for brannerite synthesis being adopted:

Brannerite was synthesised from a stoichiometric mix of ($\text{UO}_2 + \text{TiO}_2$) which was compacted and placed in a re-crystallised alumina boat. The boat was held in a Pt-wound tube furnace for 6 weeks at 1400°C under a slight

positive pressure of oxygen-free argon. The furnace was flushed with argon for 24 hours prior to heating and throughout the course of synthesis and cooling to ambient temperature.

It was suspected that the sintering temperature and the heating and cooling cycles would have had an effect on the leachability of the brannerite sinter, since it is well known that these factors have marked effects on ceramic behaviour. Often the important feature is the concentration of defects, e.g. vacancies, frozen into the structure by rapid cooling. The equilibrium value of defect concentration is a function of temperature and rapid cooling prevents condensation of these defects. To avoid this possibility, a standard heating and cooling cycle was developed:

heat to 1400°C at 25°C per hour,
synthesise at 1400°C for 6 weeks,
cool to ambient temperature at 20°C per hour.

These standard cycles also aided in preventing cracking of the mullite tube.

Lussiez et al. ⁽⁴⁷⁾ have recently shown the importance of a standard sintering cycle by considering the dissolution of a NiO sinter. Leachability was markedly influenced by sinter temperature and cooling rate, in particular (see "Results and Discussion").

All the brannerite sinters were stored, as bulk products, in a deep-freeze to avoid oxidation. Sufficient was removed for a series of leaching runs only when needed, at which time it was crushed and sieved to the required size.

Having perfected the technique of preparing pure brannerite sinters, synthesis of a doped series of brannerites was undertaken. Published literature on

brannerite gives Fe_2O_3 as the major contamination in natural brannerite, where it replaces UO_2 . Hence, it was decided to synthesise doped brannerites containing 2, 3 and 5 weight-% Fe_2O_3 .

The purest available Fe_2O_3 powder (Koch Light, $\geq 99.99\%$ pure) was used to replace UO_2 in the syntheses. In all cases, the mixtures of ($\text{UO}_2 + \text{TiO}_2 + \text{Fe}_2\text{O}_3$) powders were treated using exactly the same method as described above.

2.3. LEACHING APPARATUS AND EXPERIMENTAL PROCEDURE

2.3.1. Leaching Procedure

2.3.1.1. Apparatus

The leaching vessel consisted of a Quickfit 250 ml glass split-flask with a 5-necked, wide-flanged lid and a flanged hemispherical bowl. The two halves were connected with a metal clip. A glass paddle stirrer, attached to an overhead Heidolph variable speed motor (rotation up to 2300 rpm) via a rubber joint, was aligned through the central part by means of a P.T.F.E. sleeve guide. The stirrer guide ensured smooth stirring with no lateral movement of the paddle.

The four remaining necks were used for:

- a) holding a mercury-in-glass thermometer,
- b) holding a condenser which was essential to prevent evaporation, especially at higher leaching temperatures,
- c) holding an electrode, where appropriate, otherwise stoppered, and
- d) sampling, otherwise stoppered.

The use of a baffle was considered unnecessary due to the combined effect of an uplifting paddle and the immersed thermometer holding solid particles in suspension, in a turbulent regime.

Tight seals were maintained at all joints to prevent loss of leach solution by evaporation.

Heating was achieved by the use of a heating mantle (Electrothermal, 300 W rating), into which the leaching vessel was placed. The temperature within the flask was controlled by a "Fi-monitor" (Fison's Scientific Apparatus)

and a Variac placed in the heating circuit. Careful choice of Fi-monitor setting and input voltage to the heating mantle (typically 80 V for 75°C, 30 V for 30°C) enabled the temperature to be controlled to within $\pm 0.5^\circ\text{C}$. The vigorous stirring motion employed eliminated temperature gradients in the solution, so external insulation was not necessary.

For ease of use, the whole leaching rig was mounted on an aluminium frame on the laboratory bench.

Figure 5 shows the typical leaching set-up.

2.3.1.2. Experimental Procedure

2.3.1.2.(i) Preparation of leach liquors

All the leaching studies involved the use of acid media which were made up from standard laboratory reagents:

H_2SO_4 ; BDH Chemicals Ltd. AnalaR, S.G. = 1.84,
assay 98%, $\sim 18\text{ M}$

HNO_3 ; BDH Chemicals Ltd. AnalaR, S.G. = 1.42,
assay 69-71%, $\sim 16\text{ M}$

HCl ; BDH Chemicals Ltd. AnalaR, S.G. = 1.18,
assay 35.4%, $\sim 11.3\text{ M}$

Acid leach liquors of standard strengths, e.g. 100 g/l H_2SO_4 , were generally prepared in quantities sufficient for any series of experimental runs, to avoid variation in composition. In experiments where an oxidant was employed, the oxidant was added to the required acid just prior to the run. Analysis of the oxidant concentration was carried out immediately to ensure that the starting conditions of the leach were as expected.

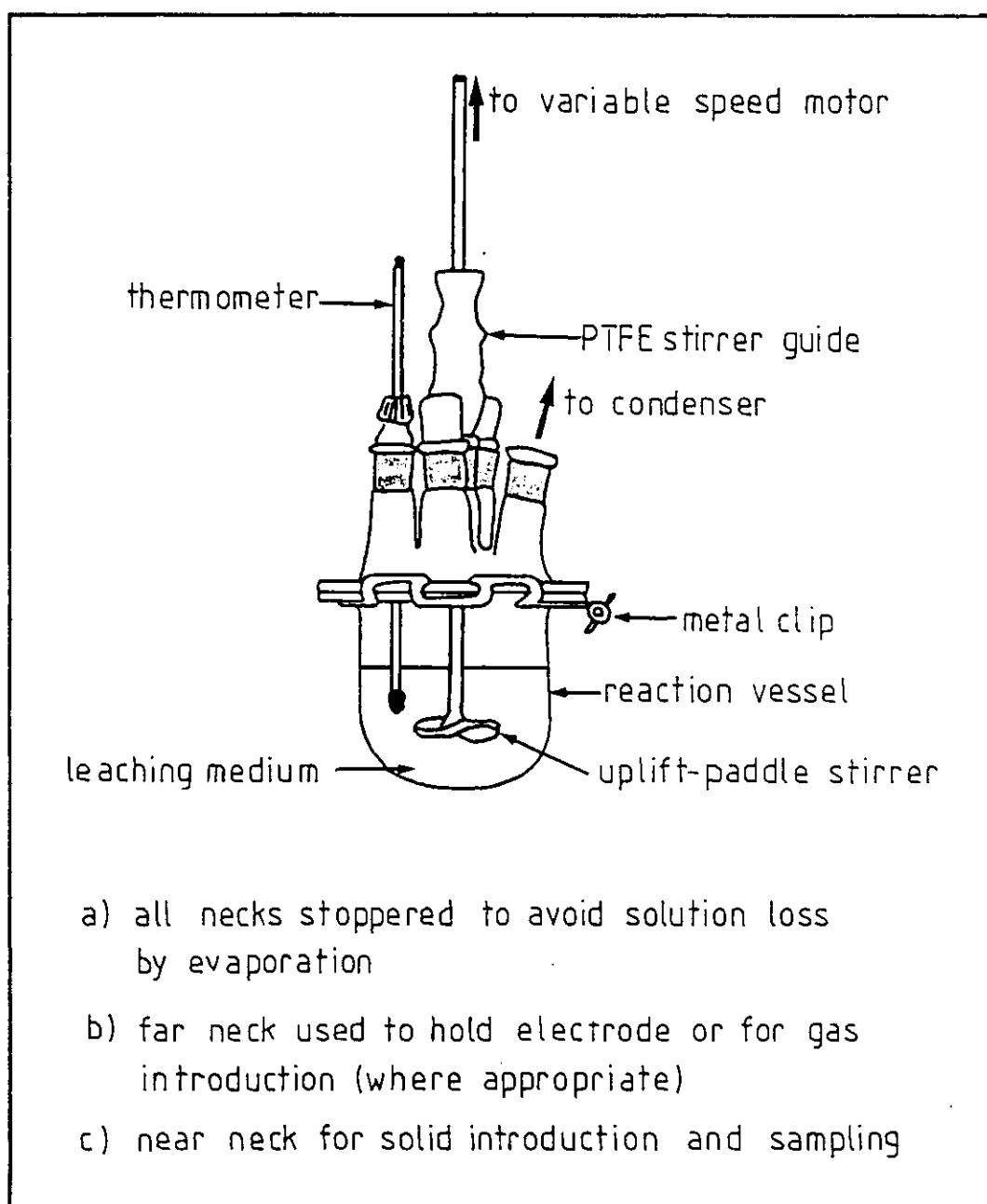


Figure 5, Schematic diagram of a typical leaching rig.

When a liquid oxidant (H_2O_2 or Caro's Acid) was used, the volume added to the initial leach liquor volume (225 ml) was small by comparison and the slight change in acid concentration was ignored. In a small number of experiments, liquid oxidant was added to the leaching system stepwise during the course of a run, usually after sampling. As hydrogen peroxide and Caro's Acid were kept refrigerated to minimise decomposition, it was assumed that there was no change in the stock concentration during any one run.

The preparation of Caro's Acid from sulphuric acid (oleum) and hydrogen peroxide invariably produces a mixture of H_2SO_5 , H_2SO_4 and H_2O_2 . In order to investigate the effect of Caro's Acid as the only oxidant, a high $\text{H}_2\text{SO}_5:\text{H}_2\text{O}_2$ ratio Caro's Acid was prepared using starting conditions as described in the Interlox booklet, "Caro's Acid Laboratory Procedure for Hydrometallurgy"⁽⁴⁸⁾. Typical preparation conditions were: $\text{SO}_3:\text{H}_2\text{O}_2 = 1.5:1$, 98 ml 30% oleum + 39 ml 80% H_2O_2 + 700-720 gm H_2O (as ice). $T < 5^\circ\text{C}$. H_2SO_5 was then ~ 1.53 M. The residual H_2O_2 concentration was then assumed to be negligible.

2.3.1.2.(ii) Preparation of solids

Two types of solid were leached, synthetic brannerite and a brannerite ore from Canada.

Synthetic brannerite was prepared for leaching by crushing a sufficient quantity of the bulk brannerite sinter, for a whole series of experimental runs, in an agate mortar. The ground mineral was sieved through 10 cm diameter stainless steel sieves to ensure that all the brannerite was ground to $-180\ \mu\text{m}$ and to give a sieve analysis. The fines fraction ($-38\ \mu\text{m}$) was removed for subsequent re-sintering. The remaining fractions were

thoroughly re-mixed for leaching, except in the case where the effect of particle size on leaching was investigated. The preparation of a bulk powder sample for a whole series of experiments, in this way, removed the possibility of variation in particle size and composition from factors affecting leaching characteristics. The long times required for brannerite synthesis and the relatively small quantities produced made it impossible for a whole series of experiments to be carried out on any particular sieve fraction and hence, use was made of powders $-180 + 38 \mu\text{m}$ in size.

The bulk powder samples were kept in tightly sealed containers in a deep-freeze, to minimise oxidation between leaching runs, and they were only removed and allowed to reach room temperature just prior to a run.

Typical solid sample weights used for leaching were 0.5, 0.75 or 1.0 gm.

Typical sieve analyses of crushed brannerites are given in Table 3. It can be seen that the brannerites were very brittle giving a very high fraction of fines, which were deemed unsuitable for leaching.

Two sets of control experiments were carried out to ensure that storage ($\approx$ possible oxidation) and thermal cycling, in cooling and warming, did not affect the leachabilities or sieve analyses of the powders. It was possible that thermal stress might have caused breaking up of the brittle particles. Sample sieve analyses and identical leaches were performed at intervals over a period of several months. Both sets of control experiments showed the sieve analyses and leachabilities of the bulk powders to be unaffected by storage and thermal cycling.

Extreme caution had to be exercised in handling the uranium mineral. All crushing and sieving activities were carried out in a draught-free area under the protection of a polythene sheet to stop the spread of dust. Protective clothing, particularly disposable gloves and a face mask to prevent inhalation of dust, was considered essential.

A 6 kilogramme sample of brannerite ore was supplied by Interlox Chemicals Ltd. from Rio Algom Ltd., Quirke Mine, Elliot Lake, Ontario, Canada. The ore was an inhomogeneous rod mill feed, so crushing and grinding was required. The particle size of this feed ranged from ~ 15 mm down to $300\mu\text{m}$, with only a small fraction of fines. The uranium content of the feed was quoted as 0.08-0.09% U.

The ore was crushed using disc-grinders of the Mineral Technology Department of Imperial College. A preliminary grind produced 95%, $-150\mu\text{m}$ material with a fine, dusty, sand-like texture. The remaining 5% was a very hard fraction with a size variation of 2.5 mm to $150\mu\text{m}$. This fraction contained some quartz-like particles, but the majority was rock-like, ranging in colour from pale green to black. The coarse material required considerable effort to grind it to $-150\mu\text{m}$.

Thorough mixing of the ore, to obtain representative samples for leaching, was achieved by placing the whole batch in a sealed, cylindrical vessel and rolling it for a period of 24 hours. This was followed by a standard "coning and quartering" technique.

Several 20 gm samples were taken and these, together with the remaining homogenised ore, were stored in a deep-freeze to prevent excessive oxidation. The 20 gm samples of ore were removed and allowed to return to ambient temperature immediately prior to leaching.

2.3.1.2.(iii) Dissolution procedure

Before an experiment, the required amount of solid was weighed to within ± 0.0002 gm of the nominal weight, using an analytical balance, and placed in a clean, dry sample tube.

225 ml of leach liquor (containing the required amount of oxidant, if any) was pipetted into the leach vessel and the stirrer motor started. The reactor was heated until a constant temperature was maintained to within $\pm 0.5^{\circ}\text{C}$ of the nominal experimental value. At this point 25 ml of liquor was removed. This aliquot was the control "initial leach liquor" for subsequent analysis.

The solid was introduced into the flask through one neck of the lid, via a funnel. If there was any evidence of solid adhering to the funnel, a small volume of leach solution was removed and used to wash the solid into the flask, so avoiding any solid or liquid loss.

5 or 10 ml samples of leach solution were taken after $\frac{1}{2}$ hour, 1 hour, 2 hours and then at appropriate intervals, depending on the length of the leach run. This periodic reduction in volume of the leach liquor was taken into account in the calculation of experimental data. The solution volume at the end of a leach run was typically 125 ml. Leaching times varied between 10 and 40 hours. To enable a clear sample of liquor to be taken, the stirrer was turned off and the solids allowed to settle for a minute or so, prior to sampling. Samples from natural ore leaching often required centrifuging and in these cases the solids were returned to the leaching flask.

In certain leach runs, solid samples were removed from the bottom of the flask using a wide bore pipette. The samples were filtered and the filtrates used as the

liquor samples whilst the solids were washed and dried for later analysis.

In some of the leaching experiments, it was necessary to leach under an oxygen or nitrogen atmosphere. The required gas entered the vessel via a tube placed through a screw-cap adapter (similar to that used to hold the thermometer), placed in one of the necks. The outlet of the tube was positioned just above the surface of the liquid and the gas escaped through the condenser. In order to eliminate air from the vessel, the pressure of the inlet gas was maintained just above atmospheric. The supply of gas was run for 1 hour prior to leaching to expel air contained within the vessel.

In experiments where an acid-bake process was employed, the solid/acid paste was introduced into the vessel using the same method as for a normal solid.

Where appropriate, the oxidation potential of a leach liquor was monitored by means of an E_H electrode, connected to a Metrohm E_H meter, immersed in the solution. The meter gave a digital display reading but for convenience a chart-recorder was incorporated into the circuit to record these values.

The electrode assembly was calibrated at ambient temperature and care was taken to correct readings for any internal electrode potentials.

At the end of the leaching time, the final liquor sample was taken and the flask allowed to cool. The contents were then filtered using a Buchner funnel and Whatman filter paper no. 1 or no. 541. The residue was washed first with stock leaching acid, then distilled water, followed by acetone and allowed to dry at room temperature. Residues were stored for later analysis.

As with uranium minerals, care was taken never to allow uranium solutions to come into contact with the skin.

In the present work, it was not intended that the effect of stirring speed on leaching characteristics would be a major investigation. However, a few preliminary runs were carried out before a choice of stirring speed for the following experiments was made.

The stirrer motor was capable of speeds up to 2300 rpm, the rotation speeds having been measured by an adjustable stroboscope.

With speeds up to ~825 rpm, it was found that the leaching rate and overall extraction of uranium increased with stirring speed. These results can be explained by the observation that increased agitation lifted more particles into suspension from the bottom of the vessel.

At speeds above ~1300 rpm, it was found that leaching rate and final uranium extraction decreased with increased stirring speed. Visual examination of the vessel showed that speeds >1300 rpm produced such violent agitation that solids were thrown out of solution and were adhering to the lid and in the necks of the flask.

At rotational speeds of 850 + 1250 rpm, experimental data showed that the leaching rate and overall uranium extraction were essentially unaltered on varying the agitation. For convenience, a rotational speed of 1000 rpm was chosen for all subsequent leaches because this was well on the "plateau" and easily reproduced and measured.

2.3.2. Methods of Analysis

During the course of the present work, the majority of experimental data were obtained by chemical analysis of

leach liquors resulting from leaching synthetic and natural brannerites. Uranium and titanium in solution were, by far, the most important factors considered and, so, detailed analytical techniques are described in the following pages.

Naturally, many other techniques were employed but most were standard chemical analyses and, hence, are only briefly outlined. References are given to the more detailed texts from which they were followed. However, in cases where standard methods were adapted or special procedures adopted, a fuller treatment is given.

2.3.2.1. Determination of uranium in solution

The method used for the determination of uranium is based on published work of Johnson and Florence⁽⁴⁹⁾,⁽⁵⁰⁾, in which uranium was analysed in various environments such as waters, ores, phosphate rocks, phosphoric acid, and thorium and zirconium oxides. A standard procedure for analysis of uranium in solution was produced from this work by Laporte Industries Ltd.⁽⁵¹⁾. G.D. Manning⁽⁵²⁾ refined the Laporte procedure for easier laboratory bench operation and this adapted version, which is detailed below, was used throughout the present work.

The method is applicable to uranium solutions arising from leaching synthetic brannerite and natural ore. Most of the complexing and reduction reactions were specifically designed for removing metal ion interference due to dissolution of ores. However, they were still necessary for synthetic brannerite leaching because of the presence of trace impurities, doping elements and oxidants.

The principle of the method is the selective extraction of uranium into an organic phase followed by colorimetric analysis. This first involved adjusting the sample solution

to exactly 2 M in nitric acid. Ascorbic acid was added to reduce cerium, vanadium and iron, to prevent extraction, and fluoride was added to complex zirconium and thorium. The uranium in solution was extracted with tri-n-octylphosphine oxide in cyclohexane and determined spectrometrically (in the organic phase) as the 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complex in ethanol, at 574 nm.

The following reagents were required and were made up as stock solutions as indicated:-

- 9 M nitric acid; dilute 1141 ml of stock HNO_3 (BDH Chemicals Ltd. AnalaR) to 2 litres with distilled water.
- 20 gm/litre sodium fluoride solution; dissolve completely 40.00 gm NaF (BDH Chemicals Ltd. AnalaR) in distilled water and dilute volumetrically to 2 litres. Store in a polythene bottle.
- 50 gm/litre ascorbic acid solution; dissolve 5.00 gm ascorbic acid (Hopkins and Williams, AnalaR) in distilled water and dilute volumetrically to 100 ml. This solution must be made up fresh each day required.
- 38.6 gm/litre tri-octylphosphine oxide (T.O.P.O.) solution; dissolve 77.20 gm T.O.P.O. (Eastman) in cyclohexane (BDH Chemicals Ltd. AnalaR) and dilute volumetrically to 2 litres with cyclohexane.
- 400 gm/litre sodium hydroxide solution; dissolve 40.00 gm of NaOH pellets (BDH Chemicals Ltd.) carefully in about 60 ml of distilled water, in a polythene beaker. Cool and dilute volumetrically to 100 ml with distilled water.
- complexing solution; weigh 6.25 gm CDTA (Aldrich Chemical Company, (1,2 cyclohexylenedinitrilo) tetraacetic acid, otherwise known as trans-1,2-

diaminocyclohexane-N,N,N',N',-tetraacetic acid monohydrate), 1.25 gm of sodium fluoride and 16.25 gm of 5-sulphosalicylic acid (BDH Chemicals Ltd. AnalaR) into a 250 ml beaker. Add 200 ml of distilled water and mix to form a suspension. Using a pH meter, neutralise the solution to pH 7.85 with 400 gm/litre sodium hydroxide solution. Dilute volumetrically to 250 ml with distilled water and mix well.

- dilute complexing solution; dilute the 250 ml of above complexing solution to 500 ml with distilled water and adjust the pH to 8.35 with 400 gm/litre sodium hydroxide solution.
- buffer solution, pH 8.35; dissolve 74.50 gm triethanolamine (Aldrich Chemical Company) in 400 ml of distilled water. Neutralise to pH 8.35 with perchloric acid ($d = 1.54$, BDH Chemicals Ltd. AnalaR) and allow to stand overnight. Readjust the pH to 8.35 with perchloric acid and dilute volumetrically to 500 ml with distilled water.
- 0.50 gm/litre Bromo-P.A.D.A.P. solution; dissolve 1.000 gm of 2-(5-bromo-2-pyridylazo)-5-diethyl-aminophenol (i.e. Bromo-P.A.D.A.P., Aldrich Chemical Company) in ethanol (James Burrough Ltd.) and dilute volumetrically to 2 litres with ethanol.
- standard uranium solution, 1000 ppm stock in ~ 0.2 M HNO_3 ; dissolve 1.0548 gm (to ± 0.0001 gm) of the purest available uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Hopkins and Williams, AnalaR) in ~ 250 ml of distilled water. Add ~ 11 ml of 9 M HNO_3 . Dilute volumetrically to 500 ml with distilled water and mix well.
- standard uranium solutions ((i) 100 ppm, (ii) 200 ppm) in ~ 0.2 M HNO_3 ; pipette (i) 50 ml, (ii) 100 ml of the above 1000 ppm uranium stock solution into 500 ml volumetric flasks. Add (i) ~ 10 ml, (ii) ~ 9 ml of 9 M HNO_3 . Dilute to volume with distilled water and mix well.

The analysis procedure could be split into two distinct steps, a solvent extraction stage and an analysis stage.

(a) Solvent Extraction:

- into a 50 ml volumetric flask
- add uranium solution to be analysed. The volume chosen should be such that the maximum uranium content is 400 μg .
- add 10 ml 9 M HNO_3 solution, mix.
- add 5 ml 20 gm/litre NaF solution, mix.
- add 2 ml 50 gm/litre ascorbic acid solution, mix.
- add 5 ml T.O.P.O. solution, shake thoroughly.
- make up to 50 ml with distilled water. Shake thoroughly for 2-3 minutes, venting the pressure as required. Allow phases to settle for at least 1 hour.

(b) Analysis:

- into a 25 ml volumetric flask
- add 2 ml of above separated T.O.P.O. solution.
- add 1 ml dilute complexing solution, pH 8.35, mix.
- add 4 ml bromo-P.A.D.A.P. solution, mix.
- add 1 ml pH 8.35 buffer, mix.
- shake thoroughly and leave for at least 1 hour to develop complex colour. Experience showed that leaving overnight is preferable.
- add 16 ml ethanol, mix.
- make up to 25 ml with distilled water and mix well.
- measure absorbance at 574 nm, in 1 cm silica cells, slit 0.10 mm, using a blue photocell.

Optical density measurements were made on a Hilger and Watts Uvispek.

In order to avoid contamination of stock solutions, volumes were not drawn directly from stock bottles, but approximate volumes needed were poured into beakers and any residues discarded.

A few notes on the indirect method:-

- to ensure quantitative uranium extraction into the T.O.P.O./cyclohexane solution, the aqueous HNO_3 concentration must be close to 2 M, so in the case of nitric acid leaching an adjustment may have to be made to the nitric acid added during analysis.
- to ensure a final single, clear, liquid phase in the colour development stage, the water/alcohol ratio must be kept within quite close limits. It is probably better to use pure ethanol rather than industrial methylated spirit, which may contain significant water.
- use the purest sulphosalicylic acid available (BDH Chemicals, AnalaR). Do not use "Aldrich Chemical Company" sulphosalicylic acid since this causes cloudiness in the final solution.

The method of analysis is one of comparison so blank samples had to be prepared from the initial leach liquors. Further, three or four standards were required per run from which the usual calibration curves of absorbance (optical density) against concentration were drawn.

It was decided that the most convenient method of delivering a reproducible volume of uranium solution was by the use of a variable, automatic diluter (Hook and Tucker

Instruments). This can deliver sample volumes of 0.02 ml to 1.00 ml, diluted with up to 10 ml of distilled water. The sample volume was chosen so that the uranium content was $\leq 400 \mu\text{g}$. Although the absolute value of the sample volume may not have been precise, it was, nevertheless, exceedingly reproducible (negligible error) which was all that was required in comparative work. Further, flushing of the P.T.F.E. tube with distilled water, between samples, was easily achieved. Blanks and standards were taken using multiples of the sample volume, so a typical analysis run would have been:-

1 ml blank leach liquor, 1 ml samples and 1 x 1 ml, 2 x 1 ml, 3 x 1 ml and 4 x 1 ml of stock 100 ppm uranium solution to give 100, 200, 300 and 400 μg U standards. The diluent volume was adjusted so that the total "uranium solution volume" never exceeded 20 ml in the solvent extraction stage.

Although the automatic diluter can deliver sample volumes in the range 0.02-1.00 ml, it was decided that the smallest practicable volume to be delivered was 0.25 ml. Thus, the method is suitable for the determination of uranium in solution in the range 0-1.6 gm/litre, without dilution. If the uranium content at the lower limit exceeded 400 μg , the leach liquor was diluted by a known factor. The automatic diluter was used or, for greater accuracy, grade A pipettes and volumetric flasks.

Typical standards used during analysis contained 100, 200, 300 and 400 μg uranium.

The repetitive addition of HNO_3 , NaF, etc. to each of the 50 ml and 25 ml flasks proved cumbersome using normal glass pipettes. It is strongly recommended that an automatic pipette, with non-wettable tips, be employed. An "Oxford Macro-Set" was used in the present work. Again, absolute volumes delivered may not have been precise, but

they were reasonably accurate (to within 2-3%) and above all reproducible, which was the necessary consideration in comparative analysis of this nature.

Grade A 2 ml pipettes were used to extract and deliver the U-containing T.O.P.O. solution. A long-stemmed 15 ml pipette was used to deliver 16 ml of ethanol from a recalibrated stem mark.

The absorbance scale on the Hilger and Watts Uvispek varied from 0 to 3.20 units which corresponded to uranium sample contents of 0-750 μg . Preliminary experiments showed that Beer's Law was obeyed over the whole range (i.e. optical density plotted against uranium concentration was a straight line). However, due to the logarithmic nature of the absorbance scale, it was considered that optical density readings above ~ 1.8 ceased to be sufficiently well defined. Hence, an upper limit of $\sim 400 \mu\text{g U}$ ($\approx \text{O.D. of } \sim 1.8$) was set for the uranium content of a sample, assuming the use of 1.0 cm silica optical cells.

A control set of experiments showed that if the spectrophotometric samples contained more than 400 μg uranium, it was possible to dilute them with ethanol, by up to a factor of five times, before measuring optical density, provided that the blank and standards were similarly diluted. Accurate results were obtained but this is not a recommended procedure. The above method of dilution was only used when an odd sample, at the longest leaching times, exceeded the nominal limit. Generally, repeat analyses were carried out with a smaller initial sample volume or after dilution of the leach solution.

No interference was experienced in uranium analyses due to the presence of various cations, arising from leaching.

The selective nature of uranium extraction by T.O.P.O. combined with the reducing, and hence suppressing, effect of ascorbic acid and the complexing effect of fluoride ions seemed to avoid interference. Any trace cation which did extract into the organic phase either did not react with Bromo-P.A.D.A.P. or was complexed by the dilute complexing solution.

Johnson and Florence⁽⁴⁹⁾ reported that only Mo would be extracted by the system in large quantities but this element does not react with Bromo-P.A.D.A.P. They further reported that no interference was observed from 20 mg of the following elements in the determination of 100 μ g of uranium: Al, As(V), Au(III), Ce(IV), Cr(III), Fe(III), Mo(VI), Nd, Pt(IV), Sb(III), Sn(IV), Th, Ti(IV) and V(V). Hence, any titanium or iron extracted from brannerite would have had no effect on the uranium reading. In addition, 500 mg of phosphate, sulphate or chloride had no effect on uranium extraction.

Many leaching runs in the present work involved the use of Fe(III) levels up to 10-15 gm/litre, as an oxidant. Johnson and Florence⁽⁴⁹⁾ reported that 500 mg of Fe(III) could be tolerated if the ascorbic acid addition was increased to 10 ml of 10% solution. A control series of experiments showed that uranium analyses were unaffected by Fe(III) levels up to 15 gm/litre and interference could be avoided above this limit by simply increasing, proportionately, the volume of ascorbic acid solution added. Naturally, blanks and standards were treated in the same manner.

The analysis procedure described tended to be a lengthy process. As a general guide, a maximum of thirty samples plus blanks and standards could be analysed over two days including all preparation times, analyses and thorough organic removal from, and washing-up of, glassware.

2.3.2.2. Determination of titanium in solution

Determination of titanium in solution proved to be practicable only for solutions arising from leaching synthetic brannerite. Natural brannerite did produce Ti in solution on leaching, which was shown by complexing with hydrogen peroxide to produce the characteristic golden yellow colour of the $\text{Ti-H}_2\text{O}_2$ complex. However, the presence of numerous other cations rendered any quantitative measurements on the small samples available totally impracticable.

Two distinct methods of titanium analysis, by a colorimetric technique and by atomic absorption spectrophotometry, were employed in leaching studies on synthetic brannerite.

The colorimetric technique used is based on that described by Vogel⁽⁵³⁾. Hydrogen peroxide produces a yellow colour with an acid titanium(IV) solution. The coloured species has been stated to be $[\text{TiO}_2(\text{SO}_4)_2]^{2-}$ or a similar ion and it has also been formulated as $[\text{Ti}(\text{H}_2\text{O}_2)]^{4+}$ or an analogous complex. With small amounts of titanium (up to 0.5 mg of TiO_2 per ml), the intensity of the colour is proportional to the amount of the element present. Comparison was made with standard titanate sulphate solutions using the Hilger and Watts Uvispek, with a blue photocell, $\lambda = 410 \text{ nm}$ and slit-width 0.15 mm. As with uranium analyses, optical densities up to 1.8 were considered accurate, which corresponded to titanium concentrations up to 120 ppm, using 1.0 cm silica cells.

A sample of known volume from the leaching of synthetic pure brannerite (i.e. no iron-doping), in the absence of Fe(III) as an oxidant, was pipetted into a 100 ml volumetric flask. The sample volume was chosen

so that on dilution to 100 ml, the titanium content was ≤ 120 ppm. Sufficient sulphuric acid was added so that the final acidity lay in the range 1.5-3.5 N. 10 ml of 3% hydrogen peroxide solution was added and the volume made up to 100 ml with distilled water. Samples were compared with standards made up in the same way containing typically 30, 60, 90 and 120 ppm Ti. The standards were prepared from a commercial 1000 ppm standard (Hopkins and Williams) using grade A pipettes and volumetric flasks. Standards were stored in tightly stoppered polythene bottles.

As the hydrogen peroxide was added in excess in analysis, the method was suitable for leach solutions arising from leaches using hydrogen peroxide as an oxidant.

Iron interferes in the colorimetric analysis of titanium because of the colour of its solution. When iron levels were low and unknown, as in the case of leaching doped brannerite in the absence of Fe(III) as an oxidant, two procedures were adopted. The iron content could be analysed by A.A. and like amounts added to standards before H_2O_2 addition, so matching the interference. However, this was a laborious and tedious method and so was used only occasionally as a check analysis, when sample volumes permitted. Alternatively, like amounts of phosphoric acid were added to blanks, samples and standards after the addition of hydrogen peroxide, to bleach the iron colour. The amount of phosphoric acid required was previously determined by adding dilute H_3PO_4 from a burette to a sample solution until the yellow colour of ferric iron was eliminated (as measured on a colorimeter). The method was shown to be suitable for solutions containing up to 40 ppm iron.

When iron levels were high and known, the standard colorimetric method could be employed provided that the blank and standards contained the same iron concentration. Typically this technique was used when leaching pure

brannerite with Fe(III) as the oxidant, up to levels of 10-15 gm/litre. However, a problem did exist in that excess hydrogen peroxide was decomposed by iron to produce oxygen bubbles in the solution. Great care had to be taken to allow these to disperse before reading optical densities. Iron did not appear to destroy the $\text{Ti-H}_2\text{O}_2$ complex.

The colorimetric technique was not suitable for solutions arising from leaching doped brannerite with Fe(III) as the oxidant. The amount of phosphoric acid required to mask the colour of ferric iron also tended to bleach the $\text{Ti-H}_2\text{O}_2$ complex. Further, iron levels could not be accurately measured by A.A. (see later text on iron analysis); thus, the method of iron additions was not available.

This last restriction on titanium analysis necessitated the use of an alternative method. The method chosen was atomic absorption spectrophotometry. In fact, this method proved to be so quick and convenient, and yet having accuracy comparable to the colorimetric technique, that A.A. became the standard method. Colorimetric analysis became secondary in importance and was mainly used for checking purposes.

Conditions of use of the atomic absorption spectrophotometer are outlined in the A.A. "Cookbook"⁽⁵⁴⁾. The instrument used was a Perkin-Elmer 272 Atomic Absorption Spectrophotometer. The operating parameters were:

Flame:- nitrous oxide-acetylene, reducing (rich, red)
 Light source:- titanium hollow cathode lamp
 Wavelength:- 365.3 nm
 Slit setting:- 0.2 nm.

For the standard conditions, the sensitivity was about 1.9 μg per ml for 1% absorption. A standard containing

120 μg per ml titanium typically gave an absorbance reading of approximately 0.28 units (48% absorption). The working range for titanium was linear up to concentrations of 200 $\mu\text{g}/\text{ml}$ in aqueous solution. Thus, standards of 40, 80, 120, 160 and 200 ppm were generally used. For titanium levels lower than 40 ppm, extra standards were required. Titanium concentrations less than 1-2 ppm were not measurable.

The effects of sulphuric acid concentration and iron concentration on titanium readings were the principal factors considered in a preliminary series of experiments. The main conclusions were:

- at sulphuric acid concentrations less than 50 gm/litre, the titanium sensitivity increased slightly with increasing H_2SO_4 and so standards had to be prepared containing the same concentration of sulphuric acid as the samples.
- at sulphuric acid concentrations greater than 50 gm/litre there was no significant variation in titanium reading with changing H_2SO_4 . Sensitivity was enhanced in comparison to solutions prepared in the absence of sulphuric acid. Standards were prepared with $\text{H}_2\text{SO}_4 = 100 \text{ gm/litre}$ as this was the most used leach liquor.
- the general effect of iron in solution was to increase the titanium sensitivity.
- at levels of 0-20 ppm $\text{Fe}_{(\text{aq})}$, solution titanium readings were unaffected by variations in iron concentration. This range of iron concentration was typical of liquors produced by leaching doped brannerite. Titanium standards did not have to be treated with iron additions.
- at iron levels of 20-100 ppm, there was a marked increase in titanium sensitivity as the concentration of iron increased. The standards had to be doped at specific iron levels.

- at iron levels >100 ppm, up to 20 gm/litre, there was no significant variation in titanium reading with varying $\text{Fe}_{(\text{aq})}$, but iron had increased the sensitivity. Titanium standards were doped with an average value for iron concentration, typically 10 gm/litre, to correspond to many leaching runs.

Titanium readings were unaffected by the presence of other oxidants such as hydrogen peroxide and Caro's Acid.

When leaching tests were carried out using hydrochloric or nitric acids, titanium standards were prepared using the required acid, concentration and iron content.

Aspirating uranium mineral leach solutions for (say) titanium analysis does incur a hazard due to the simultaneous burning of the uranium in solution. A.A. analyses must be undertaken with an efficient fume extract system, in a well ventilated room. The operator is recommended to sit as far away from the instrument as is practicable. These precautions, and in view of the fact that the uranium used was depleted, and in small quantities in solution, allowed direct analysis during the present work. The uranium had to be treated as any other heavy metal poison, with due regard for its radioactivity.

For titanium solutions with a large and/or active uranium content, it is recommended that the uranium be removed prior to aspirating. A solvent extraction method analogous to that used for uranium analysis would be suitable. The aqueous raffinate could then be analysed by A.A. for titanium. Naturally, all standards would have to be treated in a similar manner.

2.3.2.3. Other chemical analyses

Acids used in this project were standardised against "Con-Vol" sodium hydroxide solution of an appropriate molarity (typically 0.1 M or 0.4 M), using bromocresol green as an indicator.

Hydrogen peroxide in acid solution was titrated against standard ceric sulphate solution using ferroin indicator as described by Vogel⁽⁵³⁾.

Caro's Acid was analysed using the Interlox procedure outlined in "Caro's Acid Laboratory Procedure for Hydrometallurgy"⁽⁴⁸⁾. Permonosulphuric acid was reacted with arsenious oxide and the hydrogen peroxide titrated against ceric sulphate at 0°C. The excess arsenious oxide was titrated with ceric sulphate in the presence of osmic acid as a catalyst. Finally, the perdisulphuric acid was reacted with arsenious oxide at 100°C in the presence of carbon dioxide and the excess arsenious oxide was titrated with ceric sulphate. The acid content was determined by titration with sodium hydroxide to a phenolphthalein endpoint. The sulphuric acid content was calculated by subtraction of the permono- and perdisulphuric acid contents.

Hydrogen peroxide and Caro's Acid were stored in a freezer to reduce decomposition. Frequent analysis was required to ensure the accuracy of the oxidant content of leach liquors.

The iron content of solutions was found by A.A. analysis using the standard method described in the Perkin-Elmer "Cookbook"⁽⁵⁴⁾. Standards were prepared from a proprietry 1000 ppm standard (Hopkins and Williams)

using acid of the same molarity as the leach liquor. In cases where ferric iron was used as an oxidant, ferric sulphate hydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in sulphuric acid. All the iron was then assumed to be in the +3 state. Alternatively, ferric chloride/nitrate was dissolved in hydrochloric/nitric acid, where appropriate.

Iron analyses were occasionally performed on the final leach liquors resulting from leaching doped brannerite, in the absence of iron as an oxidant. It was impossible to measure the iron dissolved from doped brannerite in the presence of ferric iron as an oxidant:-

Typically the ferric iron oxidant was 10 gm/litre or 10,000 ppm. Dissolving 1 gm of 5^{w/o} Fe_2O_3 brannerite completely in 150 ml of solution would have given 223 ppm iron. Iron can only be analysed by A.A. at levels up to 5 ppm using a 4" burner (10 ppm with 2" burner), thus a dilution factor of ~2000 would have been required. Hence a comparison between original and final leach liquors after dilution would have been 5:5.1 ppm. However this represents the best possible situation. Usually <20% of the solid was dissolved during leaching, thus the comparison, after dilution, would have been 5:5.02 ppm. Possible experimental errors, such as dilution error, make such a comparison meaningless.

Oxidants such as manganese dioxide and sodium chlorate were not analysed chemically, but it was assumed that the weight required dissolved totally giving the full oxidising power indicated by stoichiometry.

2.4. SURFACE AREA MEASUREMENTS

Surface area measurements of samples for leaching studies (particularly where the effect of particle size was investigated) were undertaken, using a Monosorb (Quantachrome Instruments) of the Mineral Technology Department of Imperial College. The procedure of use could be split into five operations (simplified):

- (i) a sample of ~4 grammes of powder was degassed at elevated temperature (~250°C) for 1 hour, in a U-tube, in the instrument gas circuit.
- (ii) the sample was returned to ambient temperature with a mixture of 70% He/30% N₂ flowing through the tube. Minimal gas adsorption took place under these conditions.
- (iii) the U-tube was plunged into liquid nitrogen, at which temperature N₂ adsorbed onto the surface of the particles; He was not adsorbed.
- (iv) the sample was returned to ambient temperature by plunging the U-tube into a water-bath. The quantity of N₂ desorbed, on the rise in temperature, gave a measure of the surface area of the particles available for adsorption. The volume of N₂ was detected by the instrument and displayed on a digital read-out as an "area" in (metres)².
- (v) the instrument was calibrated by injecting, from a syringe, a preset volume of air (and hence, N₂ volume) into the circuit.

The specific surface area of the particles was the measured surface area per gramme of sample. The area represented the surface available for monolayer N₂ adsorption and not necessarily the area available for leaching. The difference depended on the relative sizes of the N₂ molecule and the leaching agent, which in the case of acid leaching might be considered to be the

hydrated proton. However, as the same material, brannerite, was used in all the leaches, the " N_2 adsorption area" might be considered to be roughly proportional to the leaching area. Hence, a representative area could be evaluated for the various sieve fractions.

This method of surface area determination is not as accurate as the B.E.T. method and absolute values must be treated with some caution. Nevertheless, the method is perfectly satisfactory for the determination of relative surface areas of various sieve fractions of the same mineral.

2.5. MICROSCOPIC EXAMINATION OF SOLIDS

Microscopic examination of the synthetic brannerites, both in bulk and powder forms, was undertaken. The purpose of the experiments was to evaluate:

- (i) the effect of doping brannerite, with Fe_2O_3 , on the microstructural characteristics of the sinter.
- (ii) the nature of the crushed powders, prior to leaching.
- (iii) the effect of leaching on the crushed sinters.

For the purpose of examination, bulk and powder samples were mounted in an araldite resin (MY753 resin + HY956 hardener, supplied by B & K Resins, Bromley, Kent, in a 5:1 weight ratio), in cylindrical mounts (1" diameter, $\frac{1}{2}$ " high). Mounting of the bulk sinters proved to be straightforward. However, the powder samples had to be sparsely distributed on a semi-set resin base before the mount was topped up with fresh araldite. Failure to follow this procedure resulted in the particles sinking through the mount, reducing adherence and increasing the likelihood of loss of particles during polishing. A fine distribution of particles also proved to be necessary since particle/particle contact again reduced adhesion to the mount, with a similar result.

After mounting, the samples were polished, by a standard metallographic technique, on a series of water-lubricated emery papers and rotating polishing wheels covered with cloth impregnated with diamond lapping compounds, of 8, 6 and 1 micron size. Extreme care was taken to ensure that undue pressure was not applied to the samples during polishing to avoid either break-up of the brittle material or distortion of the microstructure, by strain or frictional heat.

It was found that it was not possible to treat particles less than 45 μm in size, as the bonding in the

mounting resin was not sufficient to withstand the polishing procedure.

Examination was carried out using a Reichert Universal Camera Microscope and photomicrographs were processed as necessary. Particular care was taken with the powder samples to choose representative cross-sections of the particulate material, from which information on both surface topography and internal porosity could be obtained.

SECTION 3
RESULTS AND DISCUSSION

3.1. SYNTHESIS OF BRANNERITE

3.1.1. Materials For Synthesis

Tables of X-ray diffraction pattern data are given in Appendix 1. The estimated relative line intensities are coded:

s = strong
m = medium
w = weak
v = very

Plate 1(a) shows a diffraction pattern of the UO_2 used for synthesis.

Table 4 shows the approximately measured and accurately measured d-spacings of this pattern, with the estimated line intensities. Where possible, the lines have been assigned to standard A.S.T.M. patterns and relative intensities. The uranium dioxide used for synthesis appeared to be principally uranium IV dioxide, uraninite, corresponding to A.S.T.M. pattern number 5-0550. This form of UO_2 has a cubic crystal structure. The other lines can be assigned to a variety of UO_2 standard patterns, but no other single pattern predominates.

Plate 1(b) shows a diffraction pattern of the TiO_2 used for synthesis.

Table 5 shows the approximately measured and accurately measured d-spacings of the above pattern, with the corresponding line intensities (estimated). Where possible, the lines have been assigned to standard

A.S.T.M. pattern numbers and intensities. The TiO_2 used for synthesis appeared to be predominantly a mixture of synthetic rutile and anatase, corresponding to patterns 21-1276 and 21-1272. These forms of TiO_2 have tetragonal crystal structures. Also present were traces of TiO_2 , pattern 23-1446, and $\beta\text{-TiO}_2$ (high pressure form), pattern 21-1236.

Also shown, in Table 5, are a few unidentified lines of low intensity. These were probably due to unusual forms of TiO_2 or super-lattices present. It is unlikely that they were due to impurities, in view of the very low impurity levels, as analysed chemically.

Plate 1(c) shows the diffraction pattern of Fe_2O_3 used as the "impurity" in the synthesis of doped brannerite.

Table 6 gives the values as described above. The Fe_2O_3 used corresponded to A.S.T.M. pattern number 24-72. This type of iron oxide has a hexagonal crystal structure. The unidentified lines, in Table 6, correspond to other Fe_2O_3 patterns, not impurities.

Table 7 gives the various d-spacing values of lines arising from diffraction of the X-rays by the "sellotape" backing. These lines were invariably weak, but needed to be eliminated from accurate analyses.

Plate 2(a) shows the diffraction pattern of the ground and stoichiometrically mixed ($\text{UO}_2 + \text{TiO}_2$), for brannerite synthesis. This pattern was used as a standard to ensure 100% synthesis, i.e. no residual ($\text{UO}_2 + \text{TiO}_2$).

Plate 2(b) shows the corresponding mixture for synthesis of Fe_2O_3 -doped brannerite.



Plate 1, Diffraction Patterns of Materials used for Synthesis.

(a) UO_2 , (b) TiO_2 , (c) Fe_2O_3

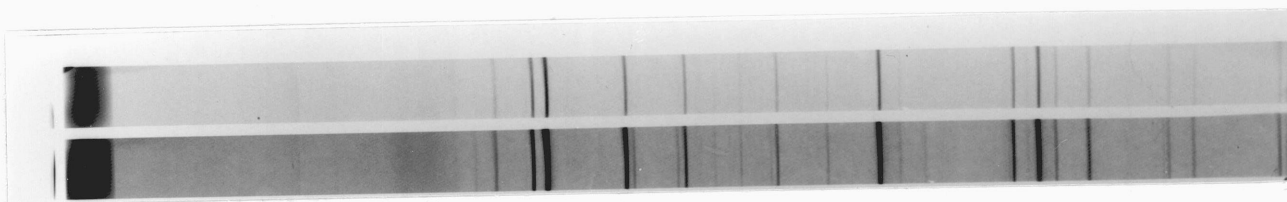


Plate 2, Diffraction Patterns of Mixes used for Synthesis.

(a) $\text{UO}_2 + \text{TiO}_2$, (b) $\text{UO}_2 + \text{TiO}_2 + \text{Fe}_2\text{O}_3$

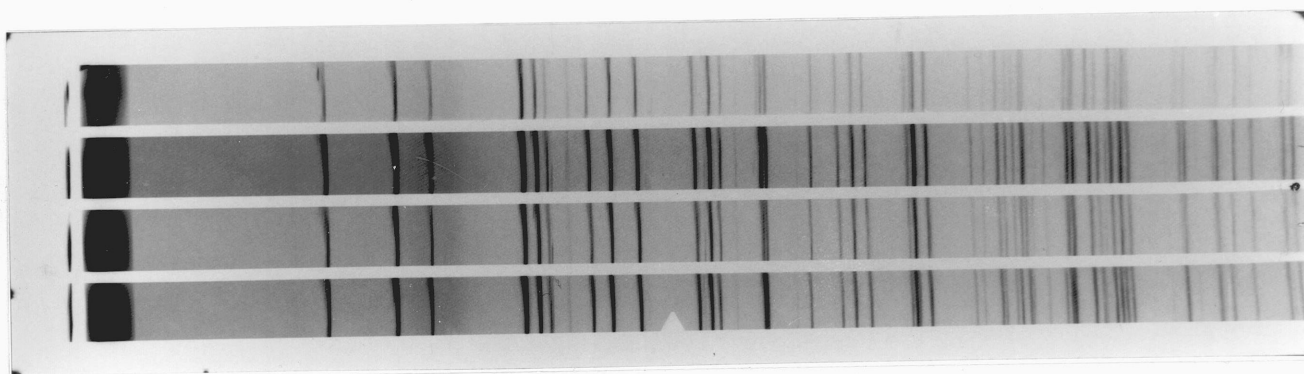
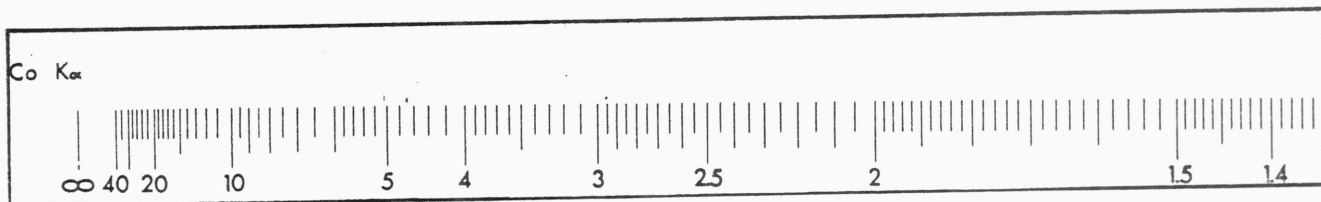


Plate 3, Diffraction Patterns of Brannerite Sinters.

(a) Pure brannerite, (b) $2^{\text{W/o}}\text{-Fe}_2\text{O}_3$ brannerite.

(c) $3^{\text{W/o}}\text{-Fe}_2\text{O}_3$ brannerite, (d) $5^{\text{W/o}}\text{-Fe}_2\text{O}_3$ brannerite.



d-spacing scale for Co $K\alpha$ radiation. (in $\text{\AA}$)

3.1.2. Various Early Attempts by Pyrosynthesis (unsuccessful)

3.1.2.1. First synthesis

- repeat of Kaiman's work,
- pyrosynthesis, 1400°C , 90 minutes, O_2 -free argon atmosphere, graphite crucible.

The synthesis had resulted in a solid, matt black and apparently homogeneous product, which retained the shape of the crucible. On sintering, there was a slight decrease in volume from the consolidated powders. The decrease in bulk volume was estimated at approximately 5%. The sinter product was very brittle and took little effort to crush and grind, to produce a fine powder, using a mortar and pestle. Examination of the bulk sinter with a hand lens showed it to be highly porous.

X-ray diffraction patterns processed from samples taken from the sinter block (centre, surface and two or three other depths) all showed an identical pattern to the original ($\text{UO}_2 + \text{TiO}_2$) mixture. No reaction had occurred, the whole sinter product consisting entirely of unreacted ($\text{UO}_2 + \text{TiO}_2$).

Clearly, a repeat of Kaiman's synthesis had not been successful and no brannerite had been formed. However, this experiment had shown that the sintering procedure, of ($\text{UO}_2 + \text{TiO}_2$) powders, did not require reaction to a ternary oxide. This confirmed the observations of various authors referred to in the literature survey. X-ray diffraction patterns are known to be sensitive down to phase concentrations of 3-5%. If sintering had occurred by chemical reaction (rather than by a diffusional-bonding mechanism), even on a microscopic surface layer scale, a new phase would have been picked up because of the very small particle size of the ($\text{UO}_2 + \text{TiO}_2$) powder mix and the consequent large surface area available for reaction, provided that:

- (i) the product did not have an identical crystal structure to one of the reactants - unlikely in view of the varying ionic radii of U and Ti;
- (ii) any product was not amorphous - this was considered highly unlikely due to the high crystallinity of the starting materials and the annealing nature of the heating and cooling cycles (i.e. slow).

Thus, it would appear that the sintering of the UO_2 and TiO_2 powders had occurred by a simple, diffusional-bonding mechanism. It was decided to pursue the pyrosynthesis route, but to increase the time held at high temperature.

3.1.2.2. Second synthesis

- pyrosynthesis, 1400°C , 24 hours, O_2 -free argon atmosphere, graphite crucible.

Again a sinter was formed, the bulk of which was identical to that produced in the first synthesis. X-ray diffraction patterns showed the mass to be composed entirely of the $(\text{UO}_2 + \text{TiO}_2)$ mix.

At the areas where the consolidated $(\text{UO}_2 + \text{TiO}_2)$ powders were in contact with the graphite crucible, a scale had formed which readily separated from the bulk of the sinter. The scale had a yellow/golden brown/grey/black banded appearance. X-ray analysis of this scale showed it to be principally UO_2 and TiO_2 , but also present were some stray, faint lines. Although these lines could not be identified exactly, they most nearly corresponded to a lower oxide of titanium, Ti_3O_5 , pattern 11-217. Thus, it would appear that the TiO_2 in the sinter mix was reduced by the graphite boat, at the temperature of the attempted synthesis.

The reduction of TiO_2 to Ti_3O_5 by carbon, at 1400°C , seems a little odd; Ellingham Diagram predictions suggest that TiO_2 should not be reduced by carbon at temperatures below about 1640°C . However, this is for the hypothetical direct reduction to Ti which, although thermodynamically feasible, is kinetically non-existent. The reduction of TiO_2 by carbon follows the energetically favourable route: $\text{TiO}_2 \rightarrow \text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO} \rightarrow \text{Ti}$. A continuous series of solid solutions occurs in the Ti-O system, which explains the reduction of TiO_2 by the graphite crucible, under seemingly unfavourable conditions⁽⁵⁵⁾.

For subsequent pyrosyntheses, it became apparent that the reactants had to be separated from the graphite crucible, to avoid the problem of TiO_2 reduction. This was achieved by holding the reactants in a re-crystallised alumina boat. This boat was placed in the graphite crucible, so that it could still act as the susceptor.

3.1.2.3. Third synthesis

- pyrosynthesis, 1400°C , 1 week, O_2 -free argon atmosphere, reactants in re-crystallised alumina boat, placed in the graphite crucible susceptor.

As before, a black sinter product was formed which was identified, by X-ray diffraction, to be a mixture of UO_2 and TiO_2 . The physical nature of the sinter was identical to that produced by the first (90 minute) synthesis. There was no sign of any brannerite lines on the X-ray pattern.

A similar scale was formed to that in synthesis 2, in areas of the sinter in contact with the alumina boat. X-ray analysis again showed ($\text{UO}_2 + \text{TiO}_2$) plus traces of a phase tentatively identified as Ti_3O_5 . As in synthesis 2,

it appeared that some of the TiO_2 was reduced by the carbon susceptor, either by diffusion through the alumina or by the transfer of volatile substances. The alumina boat showed no signs of chemical or physical change on contact with the graphite susceptor or $(\text{UO}_2 + \text{TiO}_2)$ mix.

Pyrosynthesis of brannerite clearly had not been achieved (or even shown any hopeful signs), and so a new approach, arc-melting of the reactants, was attempted.

For any solid-state reaction between UO_2 and TiO_2 to take place, intimate mixing of the particles was considered essential. The kinetics of any reaction would have been greatly affected by the degree of reactant contact. By a sintering route, the degree of contact was controlled by particle size of the $(\text{UO}_2 + \text{TiO}_2)$ mix and by compaction of the powders. It was possible that, even with the fine-grinding and cold pressing used in the attempts at pyrosynthesis, contact was insufficient to achieve reaction at a reasonable kinetic rate. It was suspected that brannerite could probably have been formed by a pyrosynthesis route by two methods. The first method was to hold the reactants at high temperature, for a long period of time. Alternatively, repeatedly grinding and reheating the product of a sintering procedure would have given fresh UO_2 and TiO_2 surfaces in contact. This should have produced a homogeneous product, but the method was considered tedious, time-consuming and it opened up the possibility of contamination.

An arc-melting route, involving the melting of one or both reactants depending on temperature, was considered to provide a means of mixing the reactants on a molecular scale, so removing any kinetic barrier to reaction. The high temperature of the arc would have also helped to enhance the kinetics of reaction, so that, provided the

reaction was thermodynamically possible at the melting temperature, it should have taken place.

3.1.3. Vacuum Arc Melting

In all cases of vacuum arc melting, the products were similar in appearance, consisting of pellets which were fully dense, shiny, black and apparently homogeneous. X-ray diffraction patterns of pellets, which had received a minimum-time melting treatment, showed principally a mixture of UO_2 and TiO_2 and only a trace of brannerite. Also present were some weak, unidentified lines which were assumed to be due to contamination from the tungsten electrode or the copper hearth.

Increasing the time at which the reactants were held molten, up to 15 minutes, gave similar X-ray diffraction patterns. There was no apparent increase in brannerite production, but the intensity of the unidentified lines was markedly increased, suggesting an increase in contamination.

Repeatedly melting and cooling a pellet gave a similar result.

To eliminate the possibility of the unidentified lines having arisen from a metastable superstructure, caused by rapidly quenching the pellet on the water-cooled hearth, a sample was annealed at 1400°C , under argon, for two weeks and cooled to ambient temperature over 3 days. The resulting X-ray pattern showed no change to that prior to annealing.

It was concluded that brannerite could not be produced in bulk by arc-melting the constituent oxides. The technique invariably produced contamination which was contrary to the fundamental object of synthesising a

"pure" brannerite. However, it was clear that arc-melting did produce an intimately mixed sample of UO_2 and TiO_2 . As an aside, a series of experiments was carried out to see if any brannerite could be formed by annealing the pellets of the UO_2/TiO_2 mixture, for varying lengths of time.

Samples of pellets with minimum contamination were annealed in a platinum-wound furnace, under argon, at 1400°C , for periods of time up to six weeks and then cooled slowly. Analysis was by X-ray diffraction. In all cases there was no change.

The total lack of success of an arc-melting route to brannerite led to an abandonment of the procedure and a resumption of the pyrosynthesis technique.

3.1.4. Successful Pyrosynthesis

- 1400°C , six weeks, O_2 -free argon atmosphere, alumina crucible in Pt-wound, horizontal tube furnace.

The product was a solid, porous, matt black, brittle sinter which appeared homogeneous. The product had retained the shape of the crucible, but there had been a marked decrease in volume from the consolidated powders. The decrease in bulk volume was measured at $\sim 11\%$. Examination by hand lens showed the sinter to be highly porous. Plate 4 shows a cross-section micrograph of the sinter bulk to illustrate the high porosity. The sinter was very brittle and was crushed, with little effort, for leaching and X-ray studies.

X-ray patterns were determined for samples taken from the surface and various depths in the bulk. All showed identical patterns which could be identified as brannerite. There was no trace of any impurity. Every

line on the film was easily identified as a brannerite line from one of the two standard patterns. On the basis that no impurity was identified, it could be assumed that the product was >95% pure brannerite.

Plate 3(a) shows a diffraction pattern of the synthetic brannerite sinter. Table 8 shows the approximately and accurately measured d-spacings of this pattern, with the corresponding estimated line intensities. These lines have been assigned to standard A.S.T.M. patterns and intensities. It can be seen that all the lines were easily identified as appearing on either or both of the 8-2 and 12-477 standard patterns. It should be noted that there is very little difference between the d-spacings on 8-2 (natural brannerite) and 12-477 (synthetic brannerite). The slight variation probably arises due to natural impurity elements. Thus, it can be concluded that a synthetic brannerite, iso-structural with naturally-occurring deposits, was synthesised by sintering the stoichiometric mix of $(\text{UO}_2 + \text{TiO}_2)$ in an alumina boat, under pure argon, at 1400°C , for 6 weeks.

The successful pyrosynthesis had confirmed the theories, of several authors, that sintering occurred without reaction to a ternary oxide and that synthesis was a two-stage process. The first stage was sintering by a diffusional mechanism, to eventually form a uniform composition, whilst retaining the original UO_2 and TiO_2 crystal structures and, hence, diffraction patterns. This appeared to be a fairly easy process due to the simple crystal structures of UO_2 and TiO_2 (cubic and tetragonal, respectively) forming regular, diffusional-path networks. The second stage was a re-ordering/reaction to form the new compound, UTi_2O_6 .

In view of the obvious porosity within the synthetic brannerite, it was decided to attempt to vacuum arc melt

the sinter in order to produce a fully dense product for leaching studies.

3.1.5. Arc Melting of Brannerite Sinter

A pellet was produced which was fully dense, shiny, black, very brittle and apparently homogeneous. X-ray diffraction analysis indicated a mixture of UO_2 , TiO_2 , brannerite and the unidentified lines previously encountered. It would appear that brannerite, on melting, had been broken down into its component oxides.

To check that the unidentified lines did not arise because of a metastable structure, an annealing test was performed, similar to that previously described. It was concluded that the pellets were contaminated on melting.

Clearly, the combination of melting and resultant contamination at $\sim 2300^\circ\text{C}$ had caused the breakdown of the brannerite structure. It was suspected that, at the melting temperature, in the presence of the contaminants, the free energy of formation of brannerite was positive, so promoting its breakdown. Quenching the sample did not allow sufficient time for the reformation process.

In an attempt to produce a fully dense brannerite, the pellet, treated as above, was held under standard pyrosynthesis conditions for two months to see if the ternary oxide could be reformed from the constituents. X-ray analysis of the product after this period showed no change.

The last result ended all possibility of forming a fully dense brannerite phase, in preference to a sinter, for leaching studies. Melting techniques were abandoned at this stage.

All synthetic brannerite samples used for leaching were, therefore, prepared by a standard pyrosynthesis route, outlined in the preceding section. The importance of a "standard" synthesis route for a mineral, on which leaching studies are to be performed, has been recently demonstrated by Lussiez and co-workers⁽⁴⁷⁾. In particular, sintering temperature and cooling rate are important because of the effects they have on the defect structure of a crystalline solid. A high sinter temperature would promote rapid attainment of an equilibrium defect structure, by diffusional processes, and the equilibrium defect concentration would be a function of this temperature. On subsequent cooling, unless the cooling cycle was sufficiently slow to maintain an equilibrium defect concentration, an excess of defects, principally point defects such as vacancies, would be frozen into the structure. The presence of such defects, especially excess vacancies, will have a marked effect in dissolution studies, by altering the electronic nature of the solid, straining the lattice and by making available extra diffusional paths.

3.1.6. Fe₂O₃-doped Brannerites by Pyrosynthesis

The 2,3 and 5^W/o-Fe₂O₃ brannerites all showed the same physical appearance as pure brannerite in terms of colour, porosity, lustre and volume reduction on synthesis. On crushing, it was noted that all the samples were brittle, but the hardness of the sinters was increased with increasing Fe₂O₃ content. Considerably more effort was required to grind the sinters of higher Fe₂O₃ content.

Plate 3 shows the diffraction patterns of pure brannerite and 2,3 and 5^W/o Fe₂O₃-brannerites, respectively.

Table 9 shows the accurately measured d-spacings of the above patterns, with corresponding estimated line

intensities. Also shown in the table are the trends of the d-spacing changes with increasing Fe_2O_3 content of the brannerite.

From Table 9, it can be seen that the general trend of d-spacings was a decrease (or no change) as the weight percent of Fe_2O_3 was increased. Only for one particular line ($d = 2.467 \text{ \AA}$) was there an increase, although a number of lines disappeared and appeared on Fe_2O_3 inclusion.

The observed decrease in d-spacing, as the presence of Fe_2O_3 was increased, indicated that the lattice spacing of the crystalline brannerite was decreasing and the presence of Fe_2O_3 was causing the structure to become more close-packed. This was not a surprising result when considering the ionic radii of the various metals present:

$$\begin{aligned} \text{U}^{4+} &= 0.97 \text{ \AA} \\ \text{Ti}^{4+} &= 0.68 \text{ \AA} \\ \text{Fe}^{3+} &= 0.64 \text{ \AA} \\ (\text{O}^{2-} &= 1.32 \text{ \AA}) \end{aligned} \quad \text{ref. Weast}^{(27)}.$$

The replacement of the relatively large U^{4+} ions by the smaller Fe^{3+} ions (as is the case in the doped brannerite) had caused the oxide crystal structure to collapse slightly. Further, the substitution of the trivalent iron for the four-valent uranium would have required vacancies in the oxygen sublattice to maintain charge neutrality, again enhancing the close-packing of the crystal structure. Furthermore, a weight/weight substitution of Fe_2O_3 for UO_2 introduced a greater number of Fe ions than U ions replaced, due to the relative atomic weights. These extra ions most probably were accommodated in interstitial sites, so reducing lattice ion diffusivity.

As there is, to date, no well defined crystal structure for brannerite, it is not possible to assign

the observed d-values to any particular crystal planes. Further, it is not possible to calculate the theoretical reduction in lattice spacing which might be expected for the various Fe_2O_3 additions.

3.1.7. Microstructures of Brannerite Sinters

Plates 4, 5, 6 and 7 show micrographs of the bulk sinters of brannerite (prior to crushing) for 0, 2, 3 and 5 weight-percent Fe_2O_3 -brannerites, respectively. Clearly, there is a marked change in microstructure with change in composition. All the samples were subjected to the same sinter processes including such factors as cold-pressing pressure, sintering temperature, time, etc., so the variation is due to composition alone.

Plate 4, pure brannerite, shows a highly porous sinter (white = brannerite, grey = araldite mount penetrating the pores, black = flaws in mount). The brannerite, in effect, forms a network of pores in three-dimensions, with a pumice-stone morphology.

Plates 5, 6 and 7 show 2, 3 and 5^w/o- Fe_2O_3 brannerites. The first noticeable feature on adding Fe_2O_3 is that the sinters are now far more solid and the density increases with increasing Fe_2O_3 . The volume occupied by the macro- and micro-pores is becoming progressively and significantly reduced and less widespread. The mineral grains appear more solid, regularly-shaped and enlarged with Fe_2O_3 addition.

Clearly, the addition of Fe_2O_3 to a UO_2 - TiO_2 sinter system had enhanced the process of sintering, to produce a more uniform and less porous sinter, with increased grain size. The mechanism by which this process had occurred was not investigated.

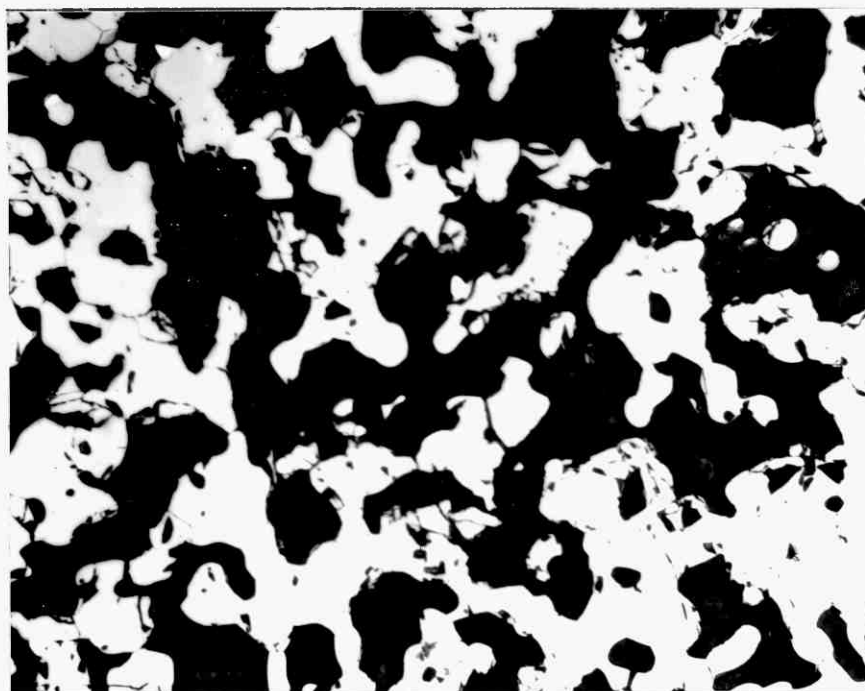


Plate 4, Pure brannerite sinter bulk. x300.

White = brannerite, grey/black = araldite penetration of pores.
Brannerite forms 3-D network of pores.

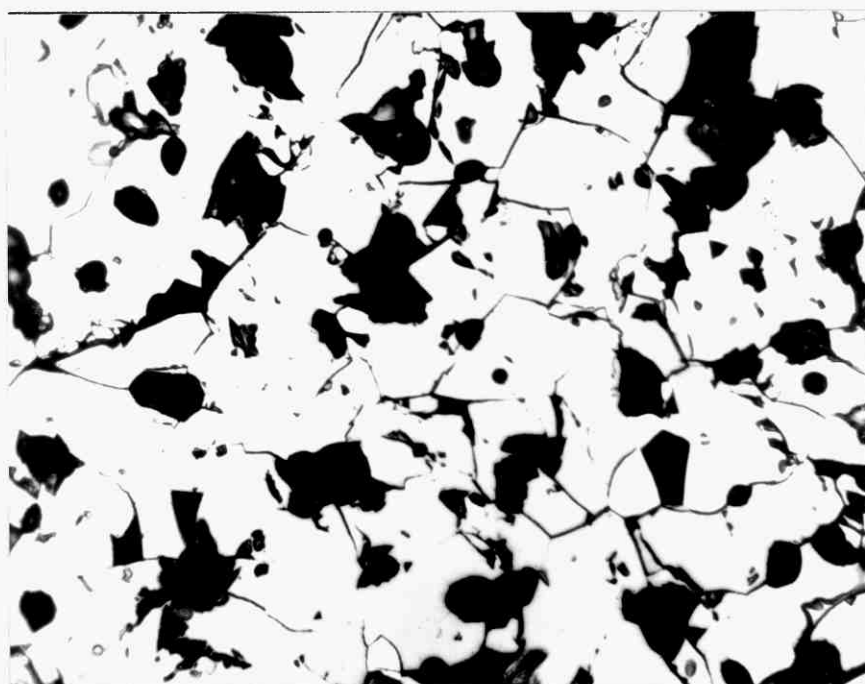


Plate 5, 2^W/o-Fe₂O₃ brannerite sinter bulk. x300.

Widespread macro- and micro-porosity. Grains of brannerite
now more solid.

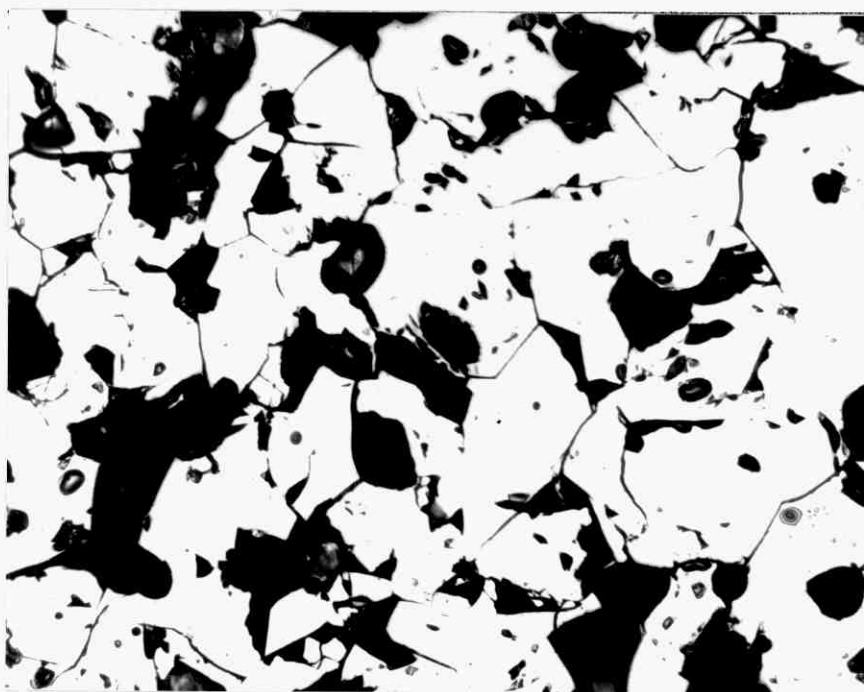


Plate 6, $3^W/o\text{-Fe}_2\text{O}_3$ brannerite sinter bulk. x300
Widespread macro- and micro-porosity, but grains increased in size, regularity and density.

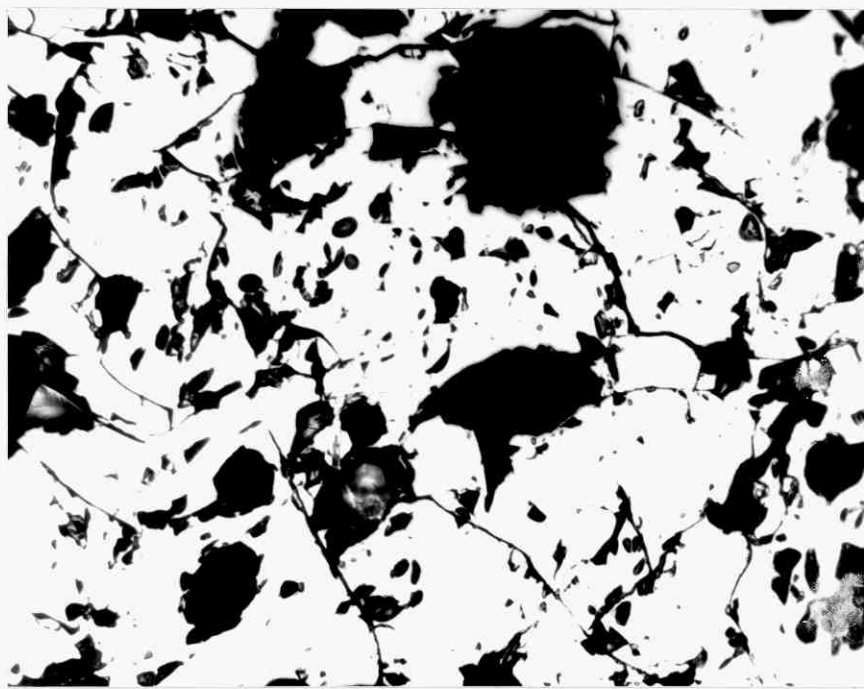


Plate 7, $5^W/o\text{-Fe}_2\text{O}_3$ brannerite sinter bulk. x300.
Porosity less widespread. Grains more regular and increased in size and density.

3.1.8. General Discussion

Although the synthetic brannerite procedures developed cannot be exactly compared to the proposed mechanisms of natural brannerite formation, namely hydrothermal and pegmatitic, the successful pyrosynthesis does have a common factor with the former. Both involved solid state diffusional processes, and the correlation gives some credence to the "Pronto-Reaction" theory.

Lack of success with melting routes casts some doubt on the pegmatitic theory, in which brannerite was formed from molten magma. However, it must be stressed that laboratory conditions could only be approximated in terms of temperature and no account was taken of the pressures involved in natural processes.

3.2. LEACHING STUDIES

Introduction

The aim of the present work was to undertake a fundamental study of the leaching characteristics of brannerite, but it was a study with an eye to the future. It is hoped that the results obtained might cast some light on the reasons why brannerite has proved to be such a troublesome mineral in the uranium industry. The object of the experimental design was to never lose sight of the fact that the leaching of brannerite is a practical problem, which requires practical solutions. It was felt that it would be pointless to carry out "artificial" leaching tests which would be totally impracticable on an industrial scale; it was important to maintain a realistic outlook in the project and not to allow it to become merely an academic exercise, which although elegant, bears little resemblance to the requirements of an industrial hydrometallurgist. For these reasons, the following parameters were considered most suitable for investigation:

- a) sulphuric acid leaching - the principal leaching medium, as outlined in the literature survey, at concentrations of 50-200 g/l.
- b) freely available oxidants - much of the literature evidence suggests that U(IV) is oxidised to U(VI), during the course of industrial leaching, by the ferric ion. Other oxidants are believed to indirectly oxidise U(IV) by a two-stage process; first oxidising Fe^{2+} to Fe^{3+} , followed by oxidation of U^{4+} by the Fe^{3+} ion. For this reason, Fe^{3+} was chosen as the principal oxidant, although other oxidants were briefly investigated.
- c) easily obtainable temperatures - most industrial uranium operations employ pachucas as leaching

vessels in which typical operating temperatures might be 70 - 75°C.

- d) particle sizes of mineral liberated by commercial crushing and grinding circuits, typically <150-200 microns.

3.2.1. SYNTHETIC BRANNERITE LEACHING STUDIES

The experimental procedure for leaching synthetic brannerite sinters has been previously discussed. The standard conditions of leaching might be summarised:

- sulphuric acid (unless stated); usually at levels of 50-200 g/l.
- temperature; 30-90°C, usually 75°C.
- 1 gm solid; -180 + 38 microns.
- 200 ml solution.
- sample by 10 ml aliquot (unless stated).
- under air (unless stated); atmospheric pressure.
- agitation; at 1000 rpm, uplift stirrer.
- oxidant; added as stated.

Exact leaching conditions are given in Tables and Graphs of results. Percentage extraction figures given refer to the removal of a metal as a percentage of the stoichiometric quantity of the element present in the mineral, and not the fraction of the total weight of the mineral. Thus, 5% U and 5% Ti extraction was equivalent to stoichiometric dissolution.

1 gramme of pure brannerite contains 553.782 mg U and 222.881 mg Ti.

Care was taken to take into account all cumulative metal removal on sampling, sample volumes and additions.

In all experiments, the leach data were applied to the various leaching models outlined in the literature survey.

It will be shown that the overall dissolution of brannerite, under any conditions (except pre-baking), was small and rarely exceeded 15%. In view of the

relatively concentrated acids employed (usually 100 g/l H_2SO_4), the change in acid concentration on dissolution was assumed negligible.

3.2.1.1. Leaching of Pure Brannerite

3.2.1.1.(i) Effect of sulphuric acid concentration

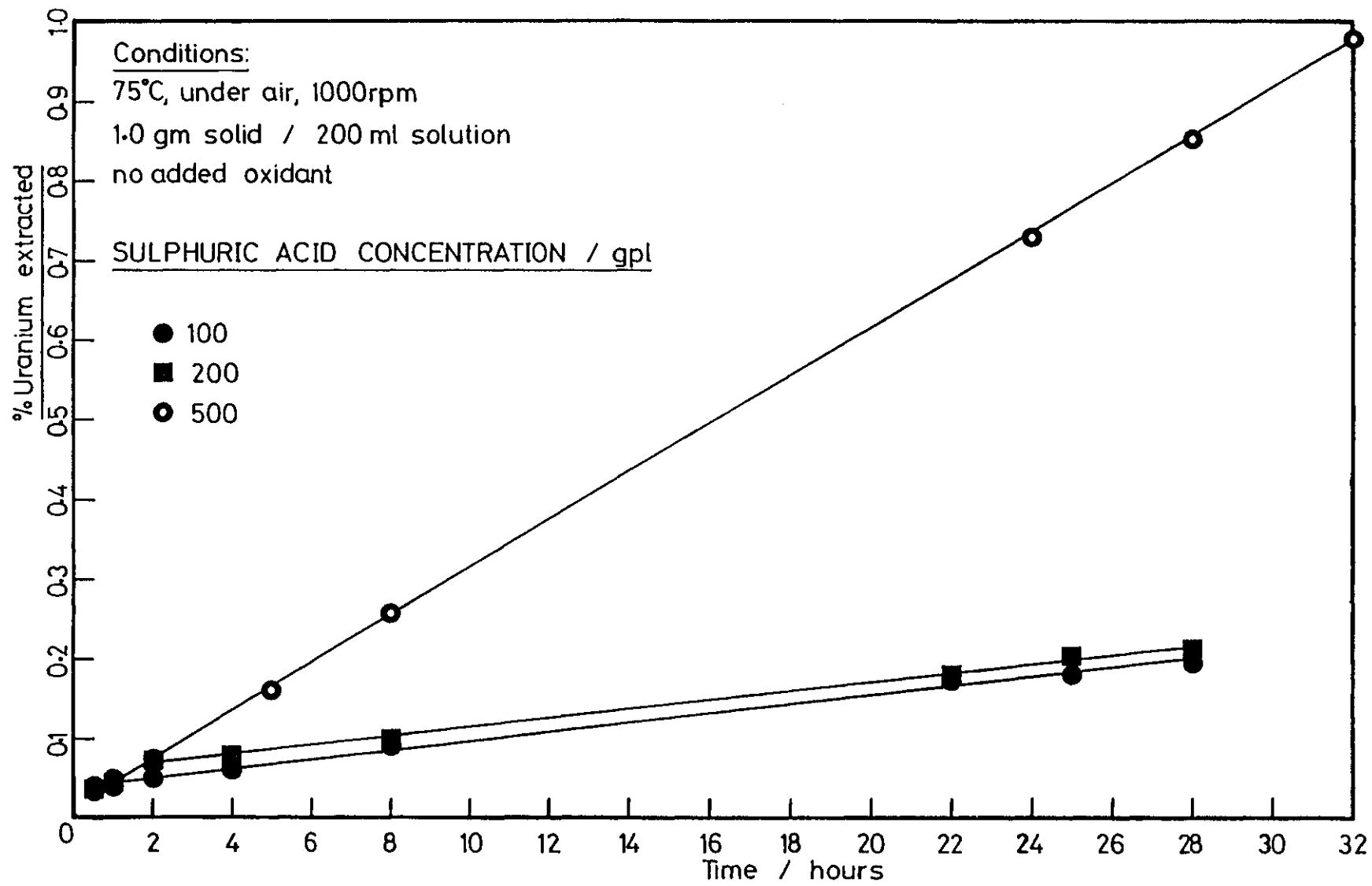
The effects of leaching pure brannerite in 100 g/l, 200 g/l and 500 g/l H_2SO_4 were studied at 75°C , in the absence of an oxidant.

Results: Table 10, Graphs 1(a), (b), (c).

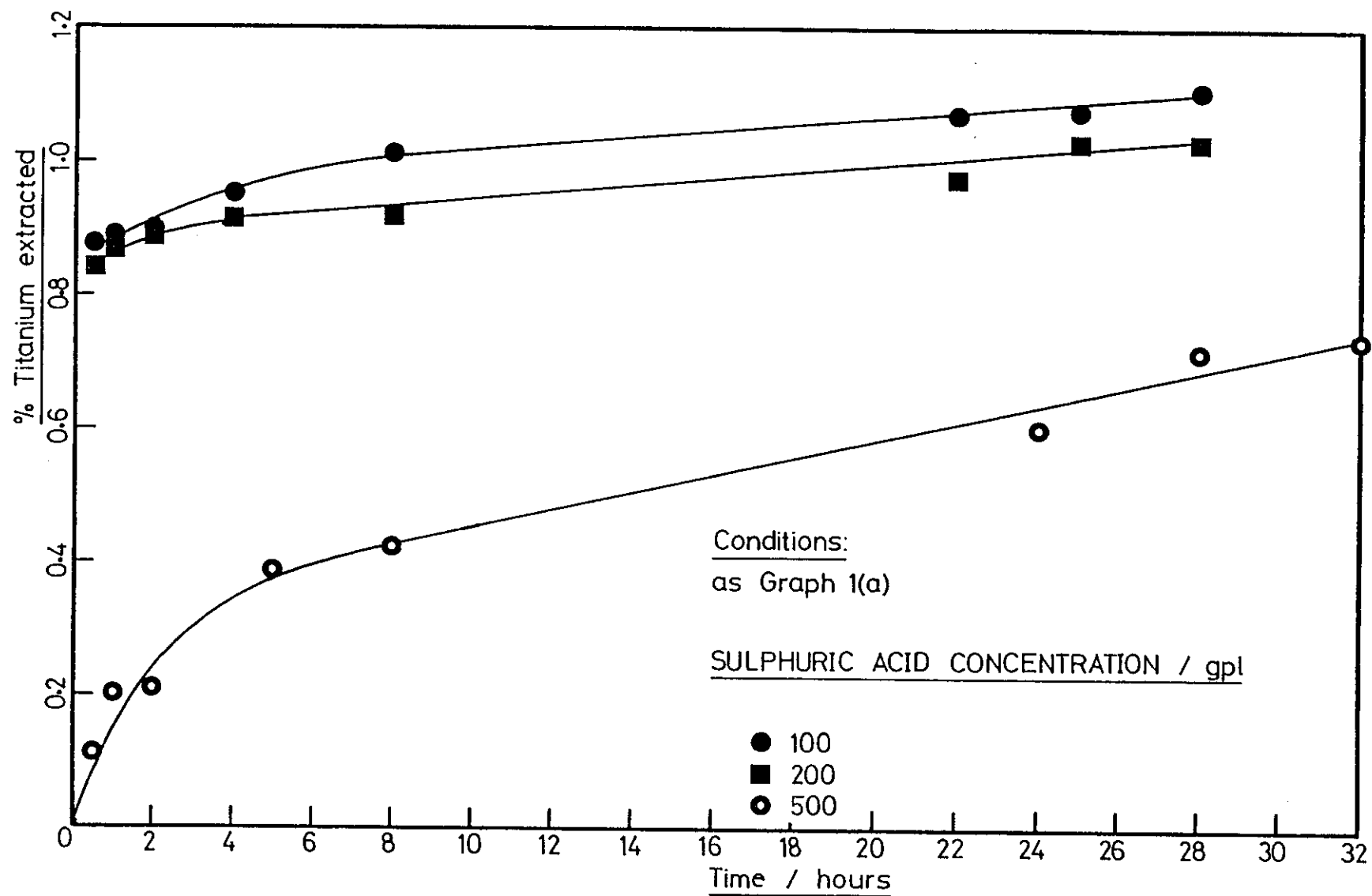
The results indicate that the mineral was practically insoluble, even at sulphuric acid levels of 500 g/l, where only 1% uranium was extracted after a period of 30 hours. Clearly, the U^{4+} ion in the mineral was not soluble under the experimental conditions of temperature, pH and E_{H} . The Pourbaix Diagram produced by Langmuir⁽¹⁷⁾, albeit drawn for $T = 25^\circ\text{C}$, suggests that under the conditions experienced, the stable soluble species requires uranium to be in the +6 valence state. The small amount of dissolution was probably due to either the presence of U^{6+} ions in the mineral or, more likely, because of limited oxidation in the agitated leaching medium.

The titanium extraction results suggest that the solubility of Ti from the mineral was also negligible, but Ti was slightly more soluble with increasing pH (i.e. lower acid concentration). The stable species in solution is the Ti (IV) valence state, the same as that held in the mineral, and so no oxidation processes were necessary.

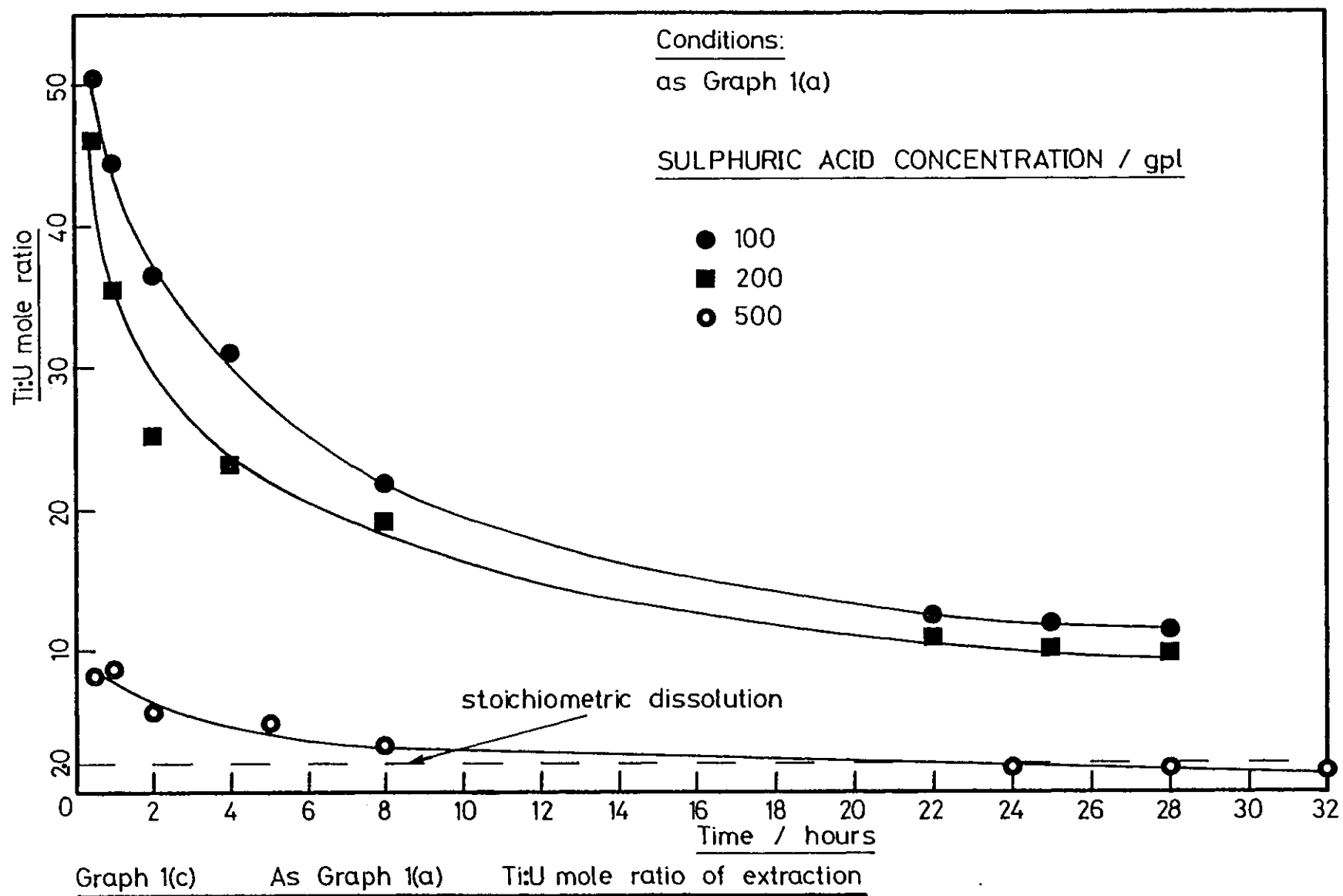
The Ti:U mole extraction ratio, ideally 2.0 for stoichiometric dissolution, showed Ti to be preferentially soluble in the early stages of leaching, possibly as an oxidation step was not required. The stoichiometric situation was only approached after considerable time when



Graph 1(a) Effect of sulphuric acid concentration on uranium extraction from pure brannerite



Graph 1(b) As Graph 1(a) Titanium extraction



the kinetics of further Ti dissolution were hampered by the presence of U-rich surface layers. Further Ti was only available for dissolution at the same rate as the U was slowly leached and it might be said that a kinetic equilibrium had been set up.

The data are found not to fit any of the leaching models and log v log plots for extraction as a function of time show a complex, varying relationship of extraction with time.

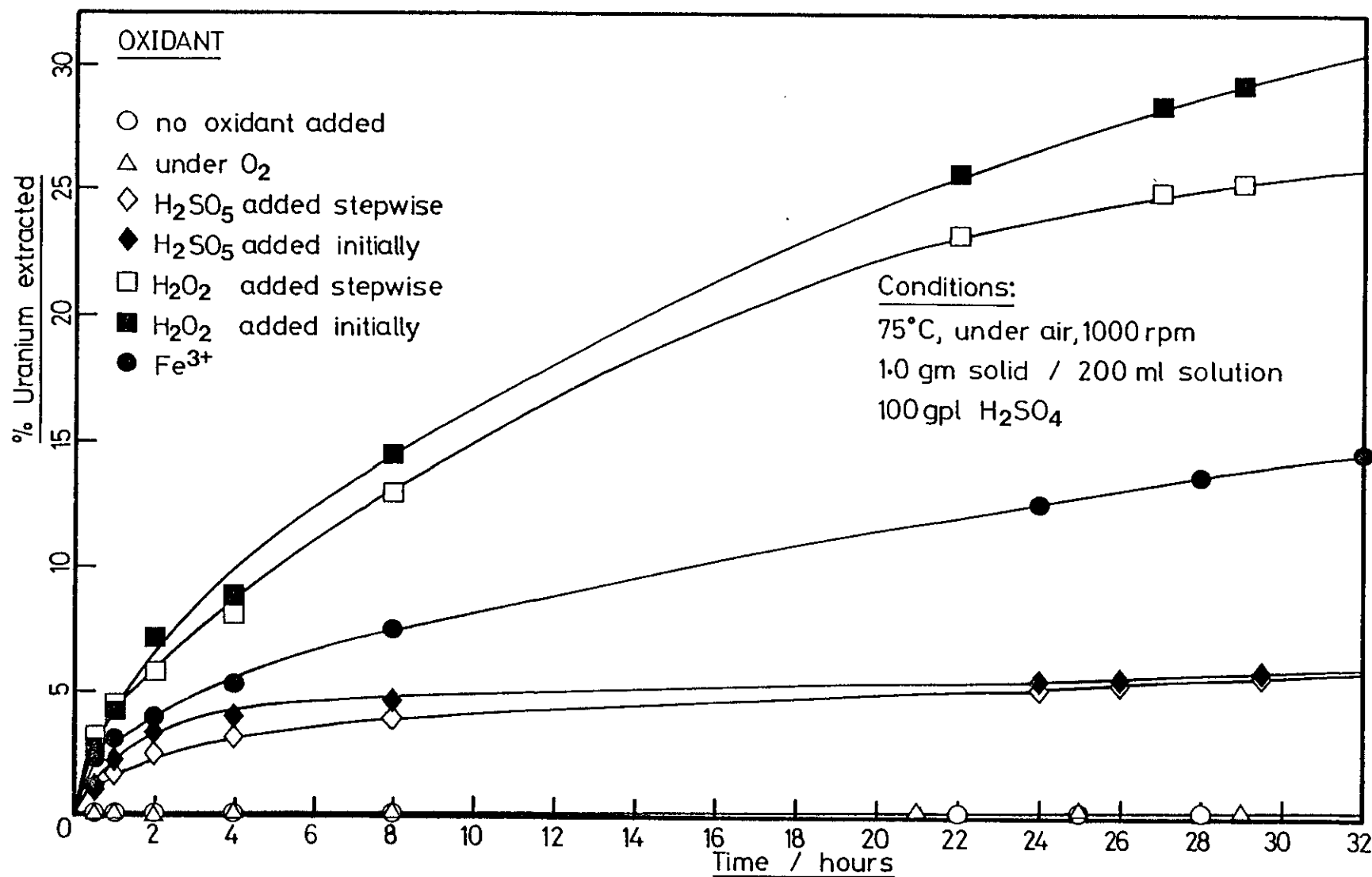
3.2.1.1.(ii) Effect of oxidant addition on sulphuric acid leaching

The effects of leaching pure brannerite in 100 g/l H_2SO_4 , at 75°C , in the presence of an oxidant, were investigated. A 'standard' oxidant presence of 10 g/l Fe^{3+} was chosen and the other oxidants added in quantities to give a total equivalent stoichiometric "oxidising power" (in terms of electron transfer), over the length of the leach. A 10 g/l Fe^{3+} concentration approximated to 8x the stoichiometric requirement to oxidise all the U^{4+} to U^{6+} in 1 gramme of mineral (in 200 ml of solution). Hence, considerable excess was present and the availability of oxidant should not have provided a barrier to dissolution.

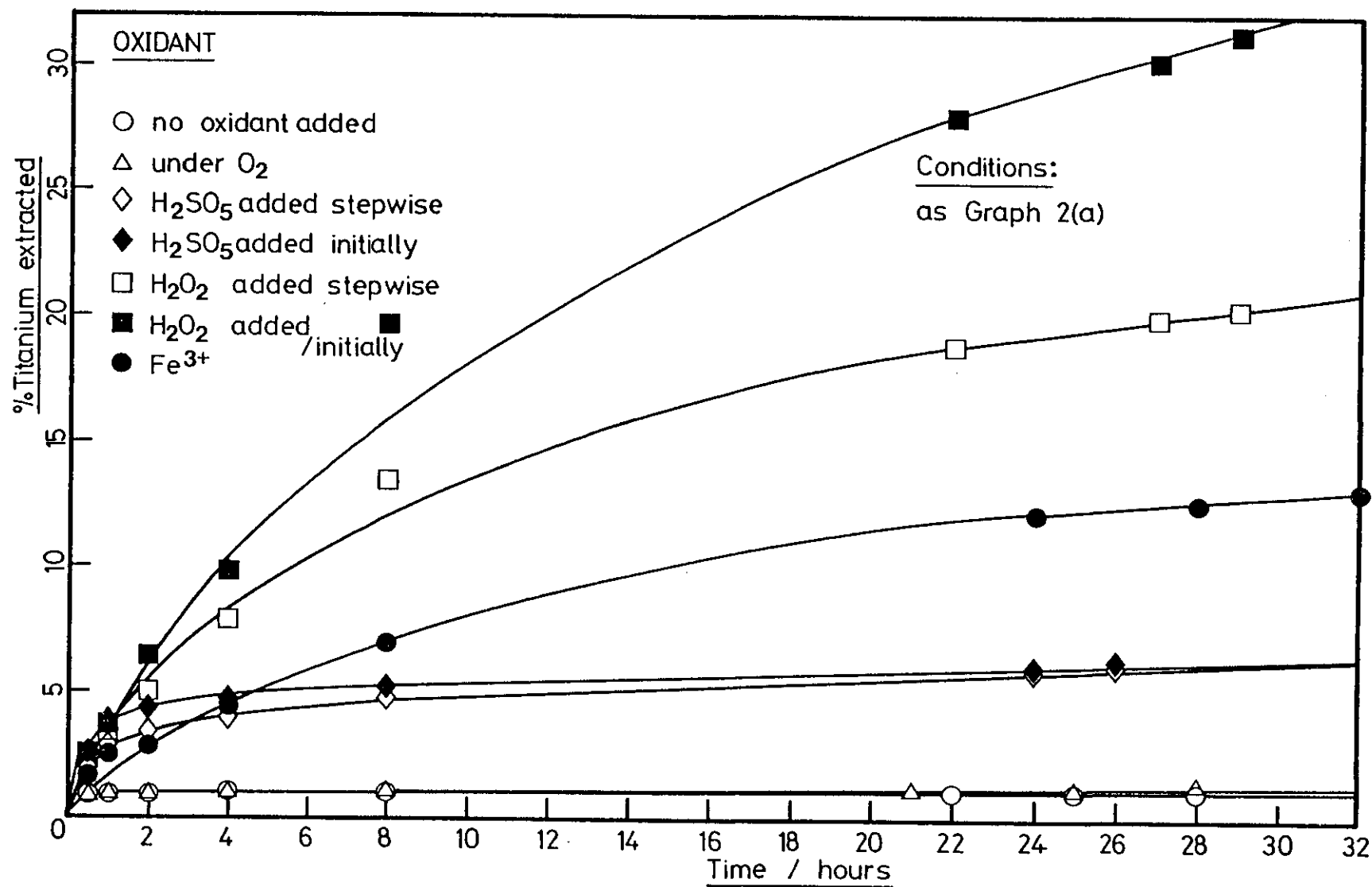
Also studied was the behaviour of brannerite on leaching under an oxygen atmosphere, although the result should not be compared with the other experiments since the oxidising power was indeterminate.

Results: Table 11, Graphs 2(a), (b), (c)

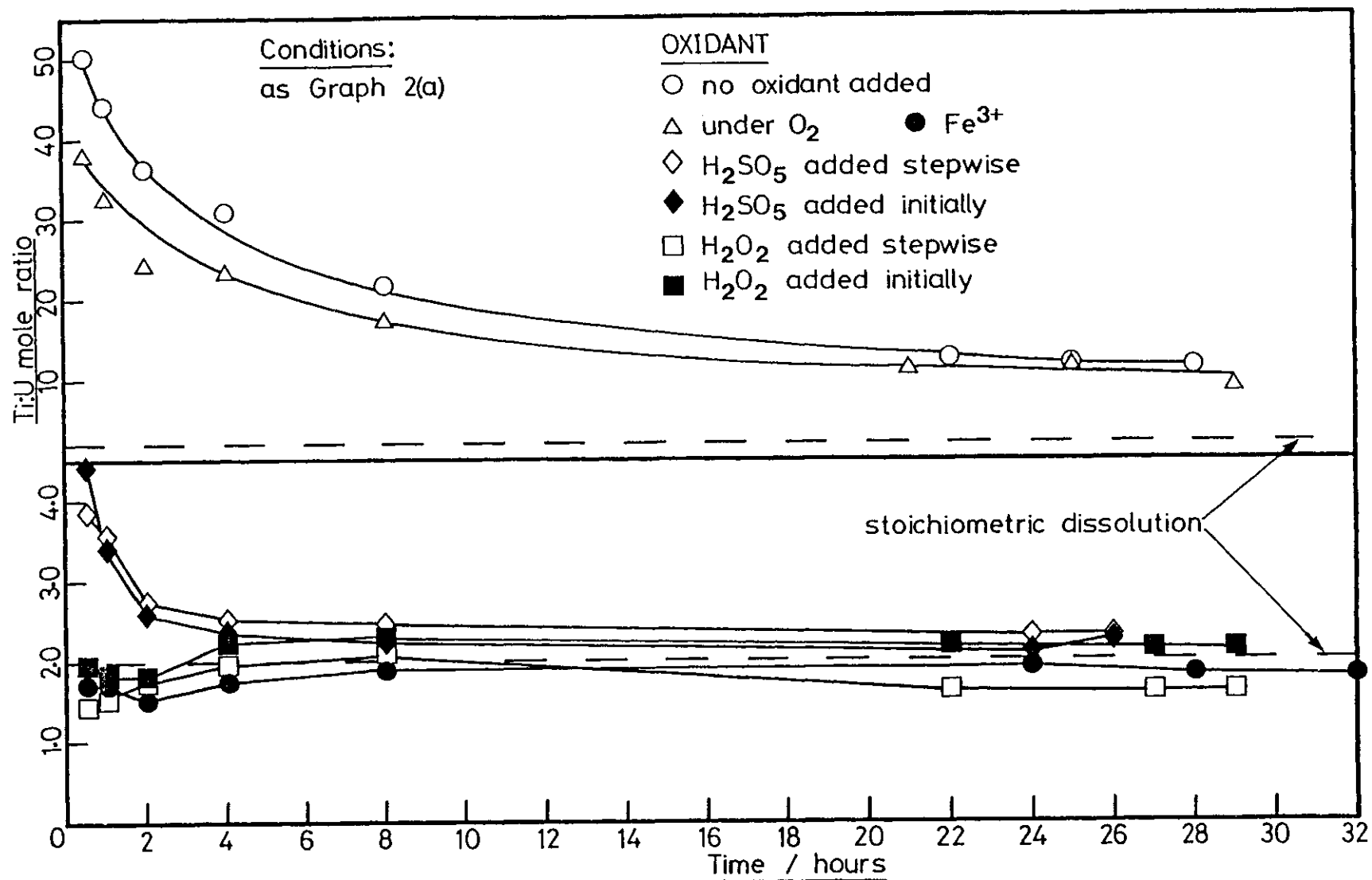
The results of the oxygen atmosphere leach show very similar characteristics to the leaches of part (i) in terms of low U and Ti extraction and a high, but decreasing, Ti:U mole ratio with time. Hence, the mode of dissolution might be argued in the same way. Clearly,



Graph 2(a) Effect of oxidant addition on sulphuric acid leaching of pure brannerite:-
uranium extraction



Graph 2(b) As Graph 2(a) Titanium extraction



the presence of an oxygen atmosphere, and the resultant high dissolved oxygen concentration, only had a marginal effect on improving the leachability of the mineral (0.26% cf 0.19%U, 1.35% cf 1.10%Ti after 30 hours).

The first noticeable effect of adding an oxidant to the leach system was that a quantitative dissolution had occurred, with uranium and titanium dissolution varying up to 30% after 30 hours. The leaching curves are similar in shape, indicating a progressively decreasing rate of both U and Ti dissolution with time.

The order of merit of the oxidising agents tested was:

$\text{H}_2\text{O}_2 > \text{Fe}^{3+} > \text{H}_2\text{SO}_5$ for equal stoichiometric oxidising power.

There was very little difference in extraction if H_2O_2 and H_2SO_5 were added as one aliquot at the start of leaching, or as stepwise aliquots throughout the leach run (added after sampling).

The initial rates of dissolution of uranium followed the order of merit of the oxidants but, in the case of titanium dissolution, the systems containing H_2O_2 and H_2SO_5 showed a very rapid initial rate (in comparison to the Fe^{3+} system). Return to the order of merit occurred after ~5 hours.

The Ti:U mole ratio plot showed the dissolution to be approximately stoichiometric after about four hours' leaching time. In the cases of Fe^{3+} and H_2SO_5 , uranium was marginally preferably soluble in the initial stages of leaching, before an equilibrium situation was set up. It might be supposed that the uranium was readily soluble, but the titanium was trapped in the Ti-oxide lattice during break-down. However, an equilibrium situation was reached when the Ti-rich surface layers hindered further U

dissolution and so the dissolution rates became complimentary to allow stoichiometric leaching. This process will be discussed later.

In the case of H_2O_2 additions to leaching, titanium was significantly more soluble than uranium in the initial stages. It is believed that the enhanced Ti leachability was a result of the strongly complexing nature of the Ti ion with H_2O_2 , so providing a driving force for dissolution. However, the kinetics of the process were slowed by the presence of U-rich particle surfaces and an equilibrium situation was reached when Ti extraction could proceed further only at the uranium dissolution rate, so producing the stoichiometric, equilibrium nature of later leaching.

Analysis of the leach liquors at the end of the leaching times, for the cases of H_2O_2 and H_2SO_5 , showed that there had been negligible decomposition of the oxidant and any change in the levels of H_2O_2 and H_2SO_5 could be explained in terms of the oxidation of the uranium dissolved.

The leaching data do not fit the shrinking core models. There is some evidence that, in the cases of H_2O_2 , Fe^{3+} and H_2SO_5 additions to acid leaching, the data show a strong correlation to the mixed kinetics model (outlined in the literature survey), for U extractions after ~ 4 hours; that is, once an approximately stoichiometric leaching situation had been established. This indicates that the uranium extraction process was not a simple diffusion or chemical controlled reaction, but a mixture of the two. This observation is further investigated and examples given in later discussion.

Log-log plots show the order of reaction (n) to have varied throughout the course of leaching, which suggests that there is no simple relationship, of extraction as a function of time, to describe the observed leaching characteristics.

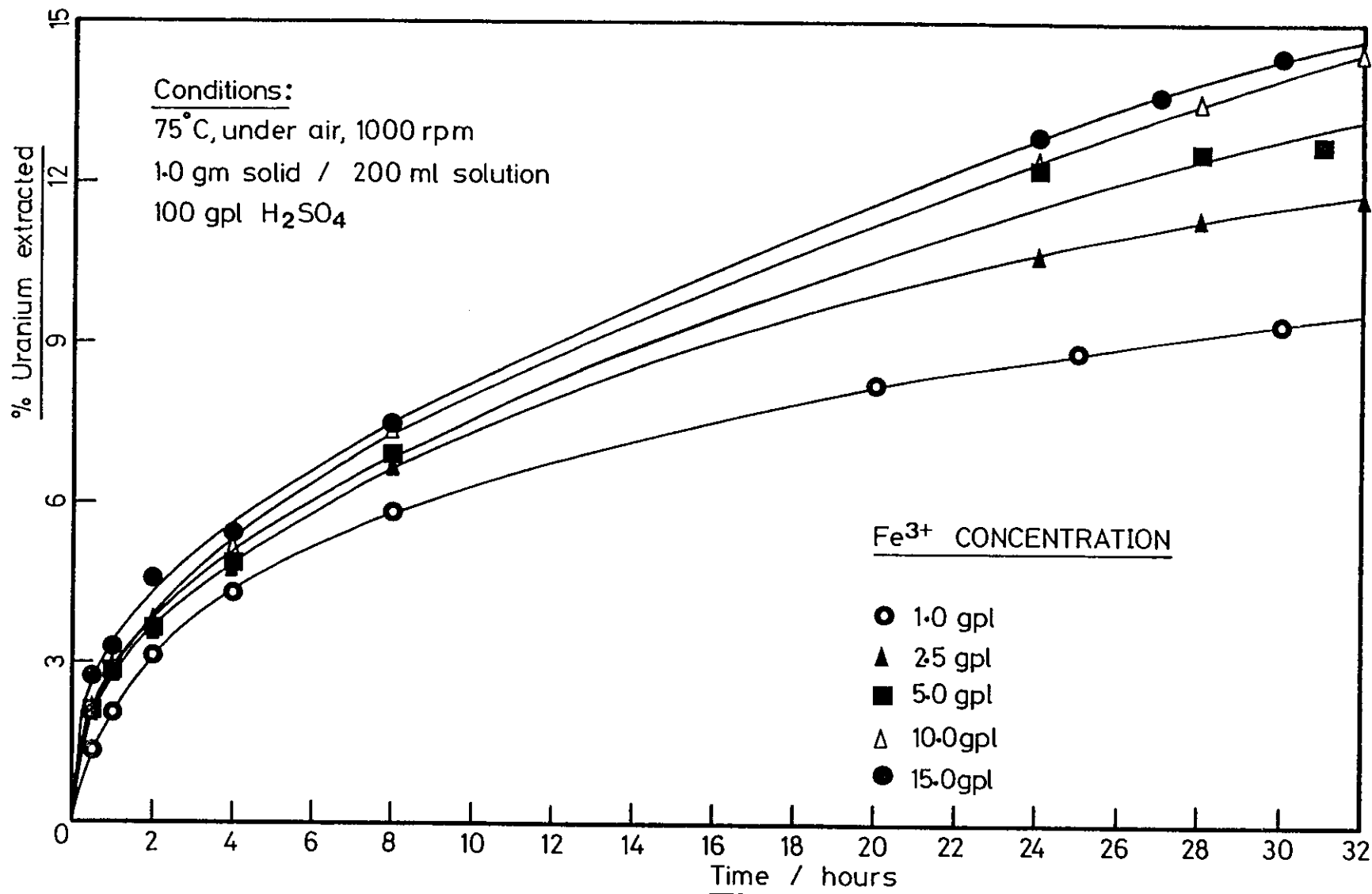
3.2.1.1.(iii) Effect of varying oxidant concentration on sulphuric acid leaching

The effects of leaching pure brannerite in 100 g/l H_2SO_4 , at 75°C , in the presence of varying concentrations of oxidant, were studied. The oxidant chosen for investigation was the ferric ion to imitate, as nearly as possible, actual leaching conditions. Concentrations of ferric ion from 1 to 15 g/l were employed. The lower end represented approximately the stoichiometric requirement for total U^{4+} to U^{6+} oxidation, of the uranium contained within the mineral sample, whilst the other extreme represented a massive overkill to remove any oxidant availability problems. The iron was added as ferric sulphate to avoid introducing other anions into the system, although the effect of increasing the sulphate concentration was considered negligible and not investigated separately. It was assumed that, under the conditions employed, the iron was present in solution as the ferric species and any presence of Fe^{2+} was regarded as minimal.

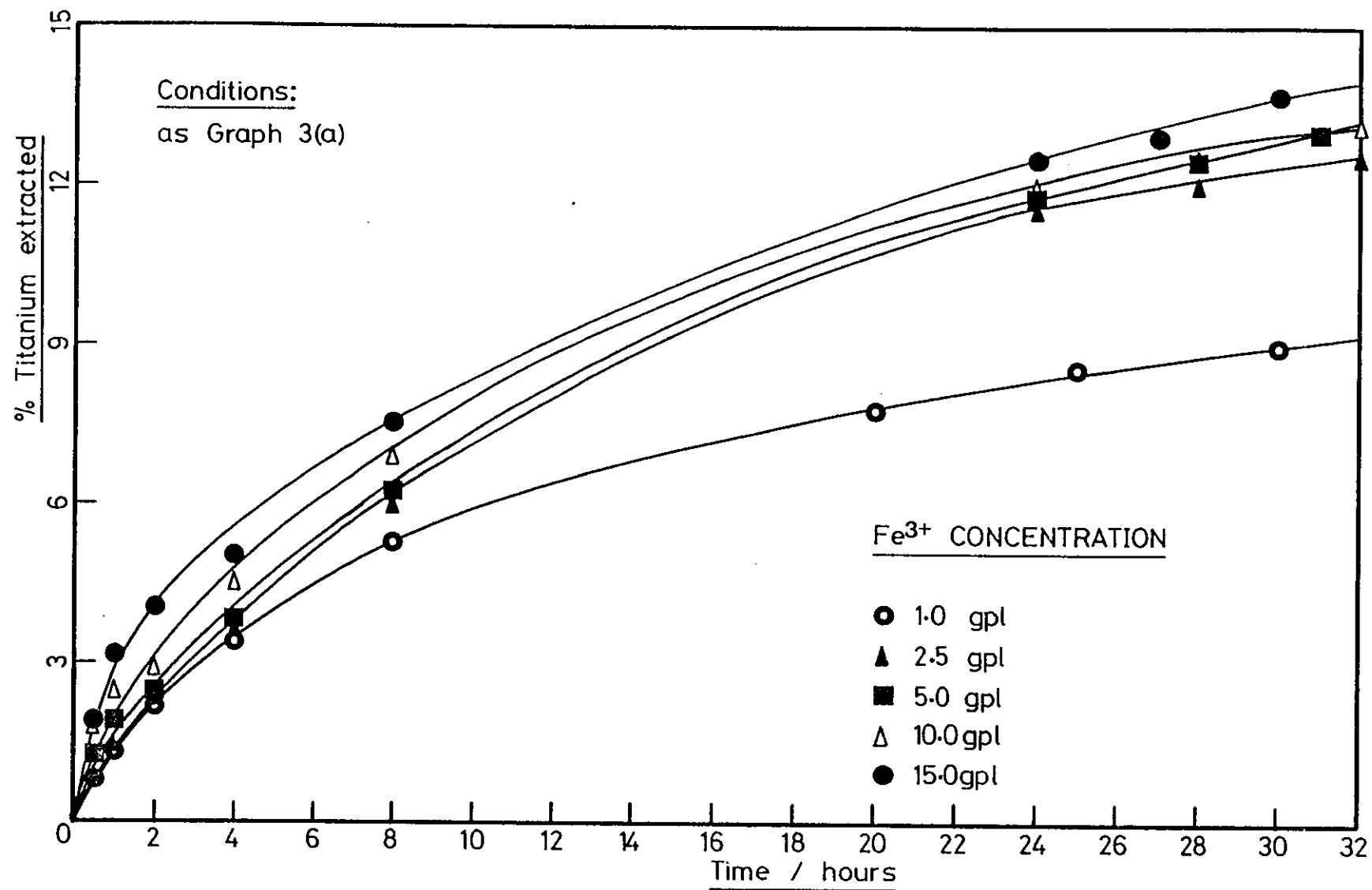
Results: Table 12, Graphs 3(a), (b), (c).

The plots of U and Ti dissolution show similar characteristics of progressively decreasing rates of dissolution. Increasing the Fe^{3+} concentration from 1.0 to 2.5 to 5.0 g/l achieved a significantly higher rate and overall dissolution of the mineral. However, further doubling and trebling the ferric ion concentration had an insignificant effect on the leaching characteristics. Hence, it might be concluded that a ferric ion concentration of greater than 10 g/l does not warrant the extra reagent costs, in terms of gain in mineral dissolution.

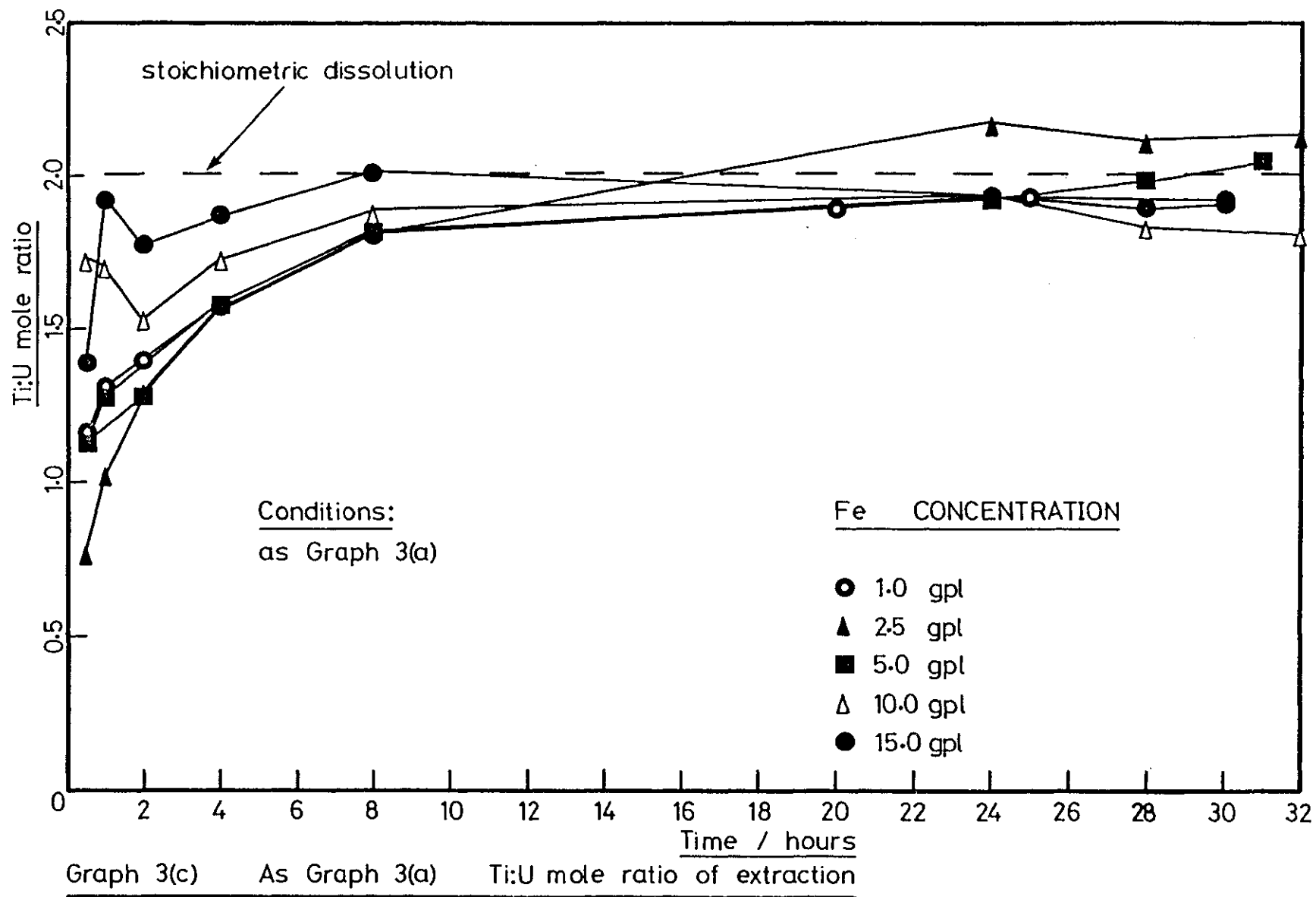
The Ti:U mole leaching ratio shows that, after the initial stages of leaching, the dissolution was approximately stoichiometric. However, in the early stages, uranium was preferentially soluble by the oxidation process with Fe^{3+} . It can be envisaged that the Ti ions were less soluble as



Graph 3(a) Effect of varying oxidant (Fe^{3+}) concentration on 100gpl H_2SO_4 leaching of pure brannerite:- uranium extraction



Graph 3(b) As Graph 3(a) Titanium extraction



they were trapped in the oxide lattice, as it broke down, on uranium removal. The Ti-rich layers would have presented a barrier to further U dissolution and so a stoichiometric equilibrium dissolution process was reached, in which the rate of U removal was governed by the availability of the U ions, as determined by the Ti removal rate. Again, this process is discussed later.

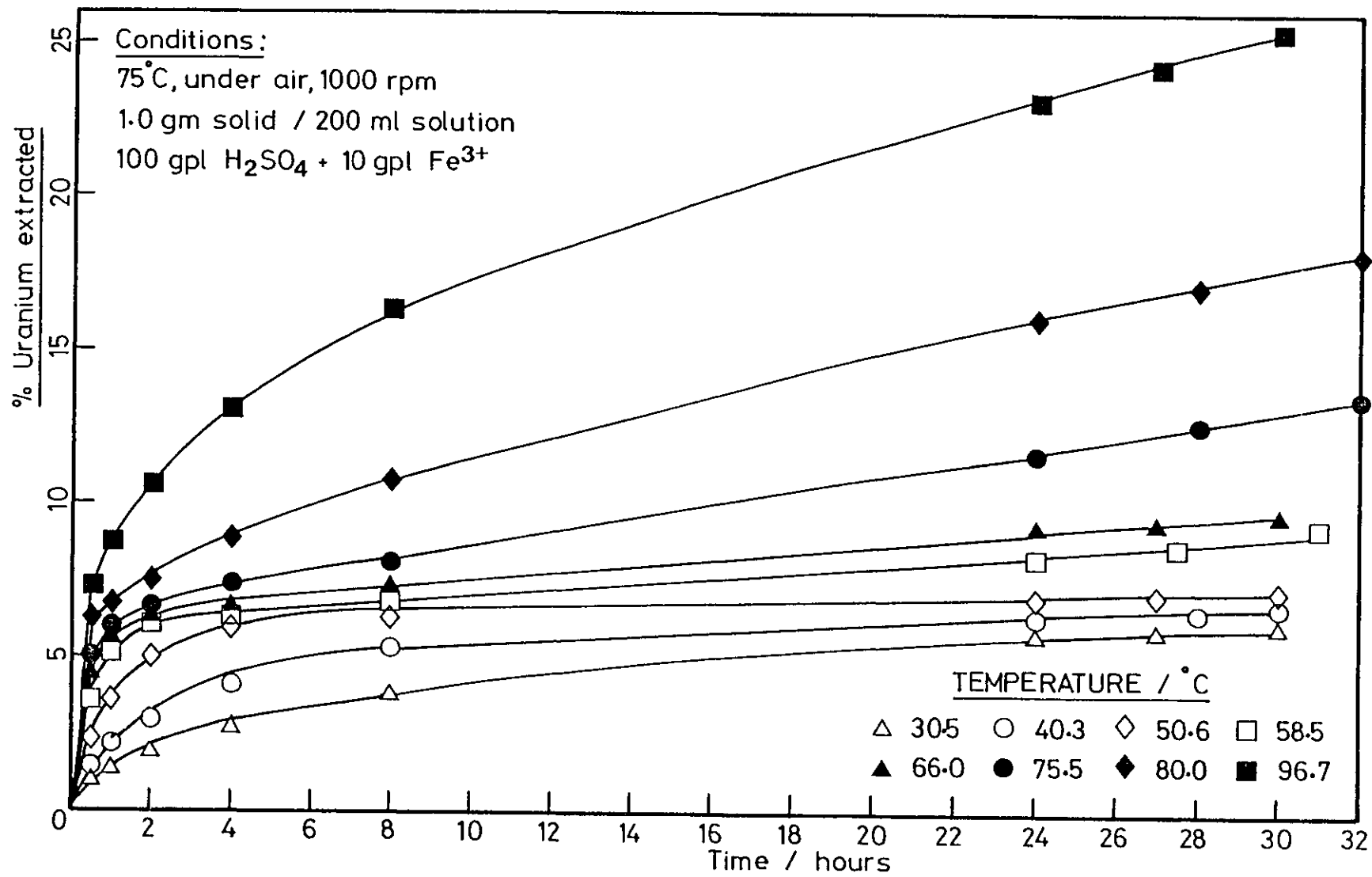
The data do not fit the two shrinking core models of dissolution. The uranium extraction values do fit the model for mixed surface reaction and diffusional control of the leach process, over the whole range of time investigated, except in the case of 1 g/l Fe^{3+} leaching where, perhaps, an equilibrium regime had not been established in the leaching time. Although the graphs are not plotted here, examples are given later with a discussion. The Ti data show no correlation. Log-log plots provide no useful information.

3.2.1.1.(iv) Effect of temperature

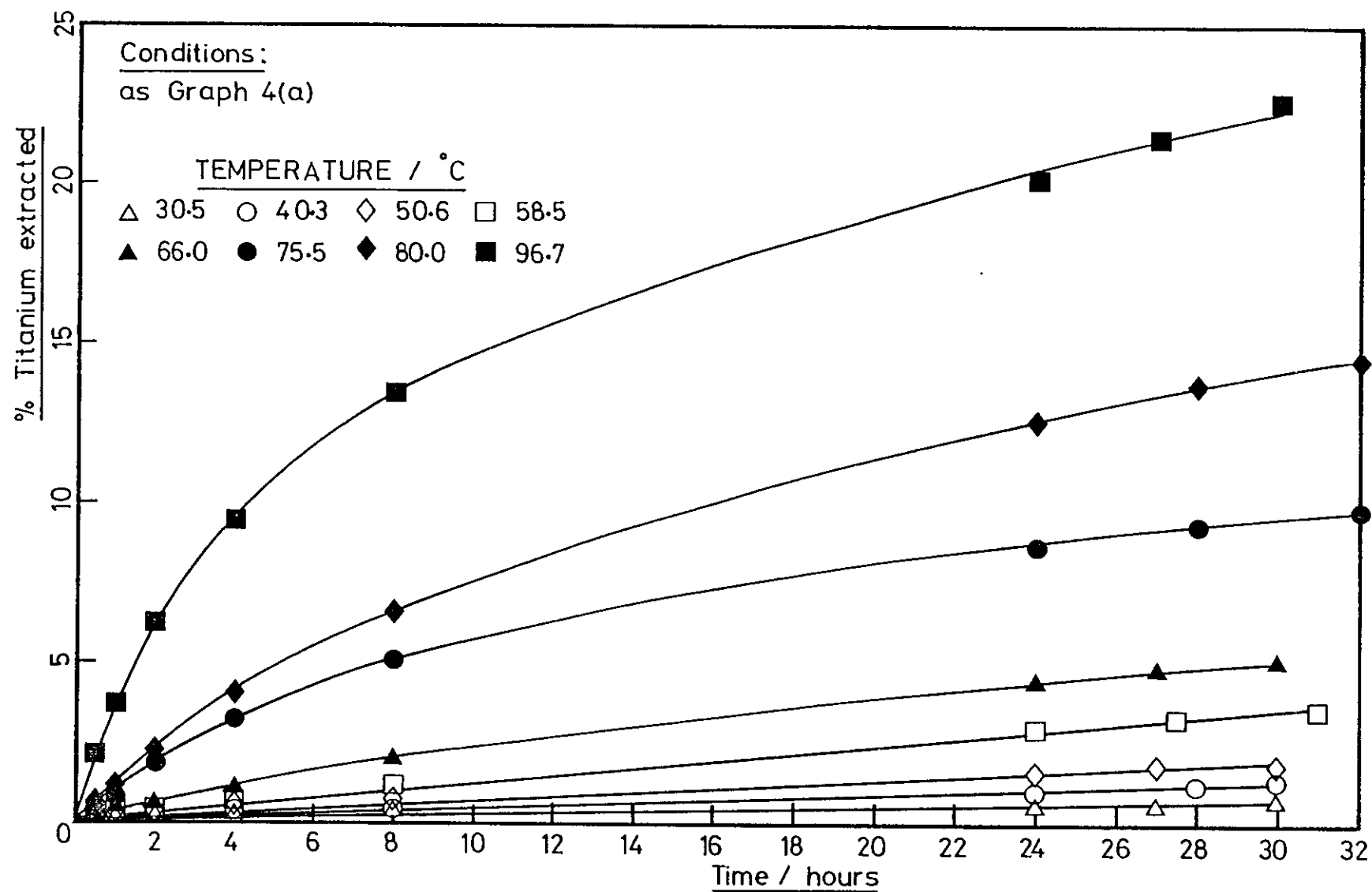
An investigation was made into the effects of leaching pure brannerite in 100 g/l H_2SO_4 containing 10 g/l Fe^{3+} as an oxidant (to produce maximum leaching power), under varying conditions of temperature, from 30°C to 95°C. The limits were chosen as being representative of the whole range of normal operating temperatures, from ambient to just-below-boiling, under atmospheric pressure. Clearly, leaching at the boiling point would have introduced problems of a three-phase system (solid/liquid/vapour) and higher temperatures would have required the use of an autoclave.

Results: Tables 13(a), (b), (c). Graphs 4(a), (b), (c), (d), (e).

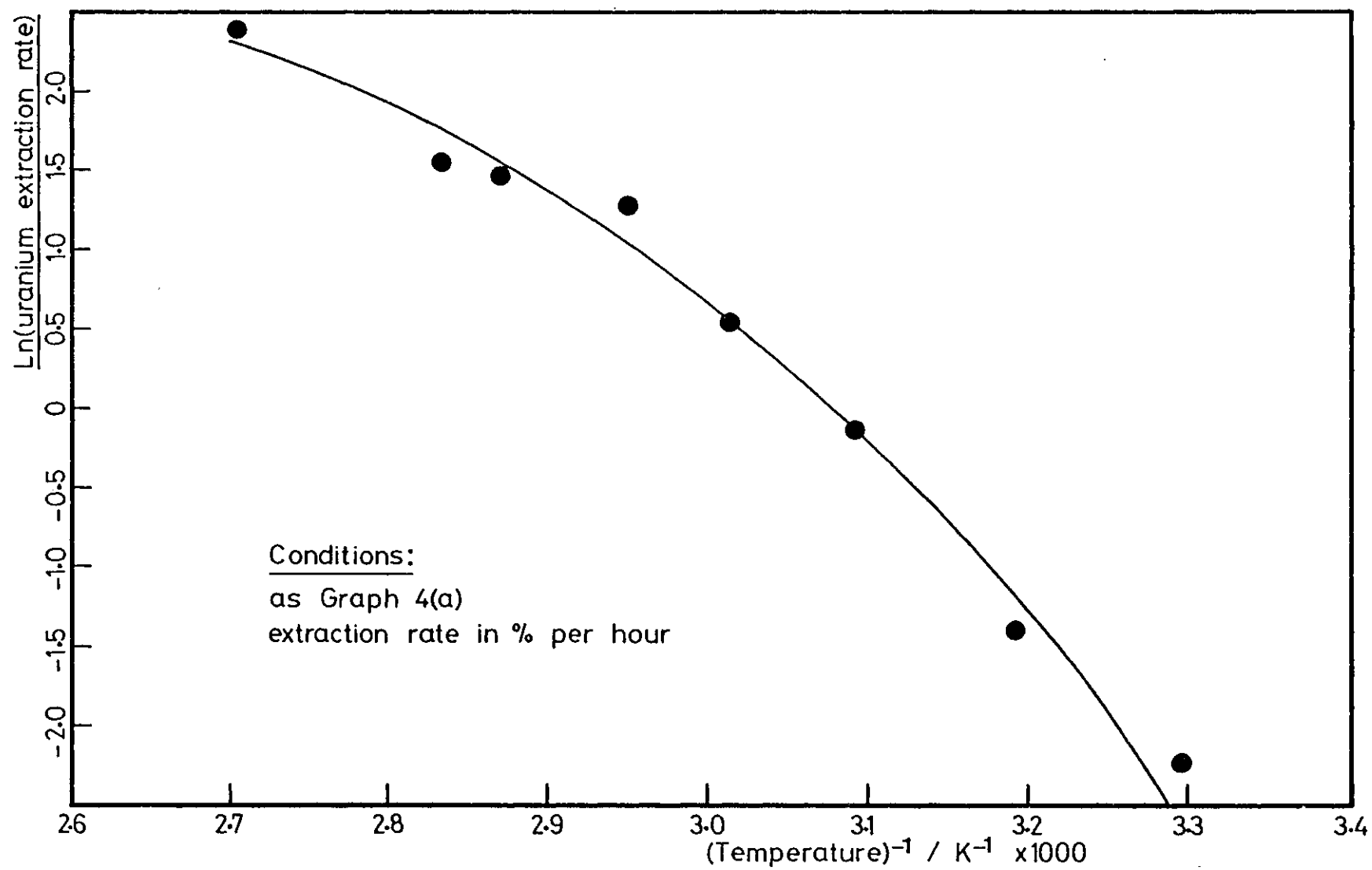
Graphs 4(a) and 4(b) show that the curves of extraction of uranium and titanium, respectively, as a



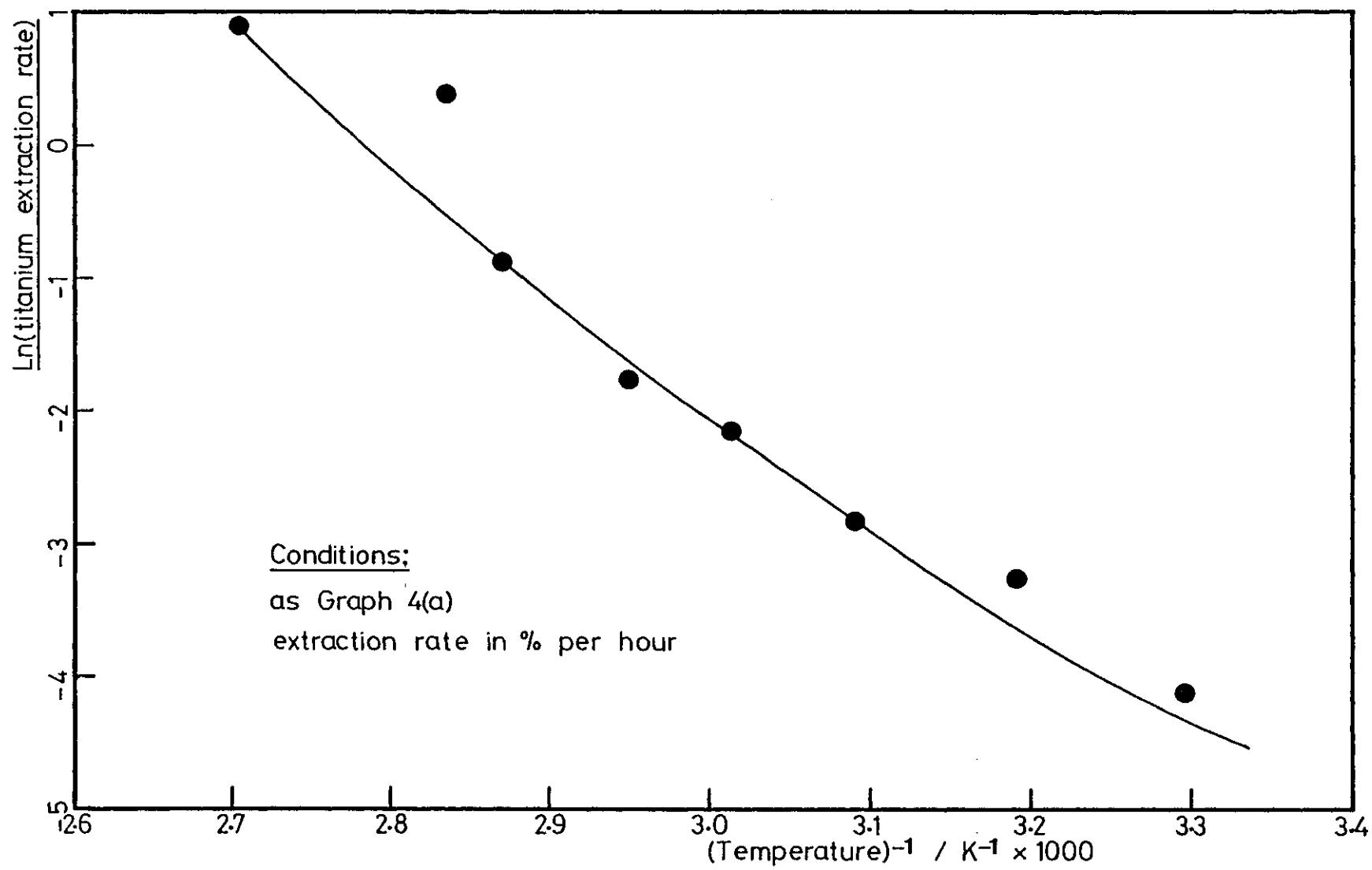
Graph 4(a) Effect of temperature on leaching pure brannerite in 100gpl H_2SO_4 containing 10 gpl Fe^{3+} :- uranium extraction



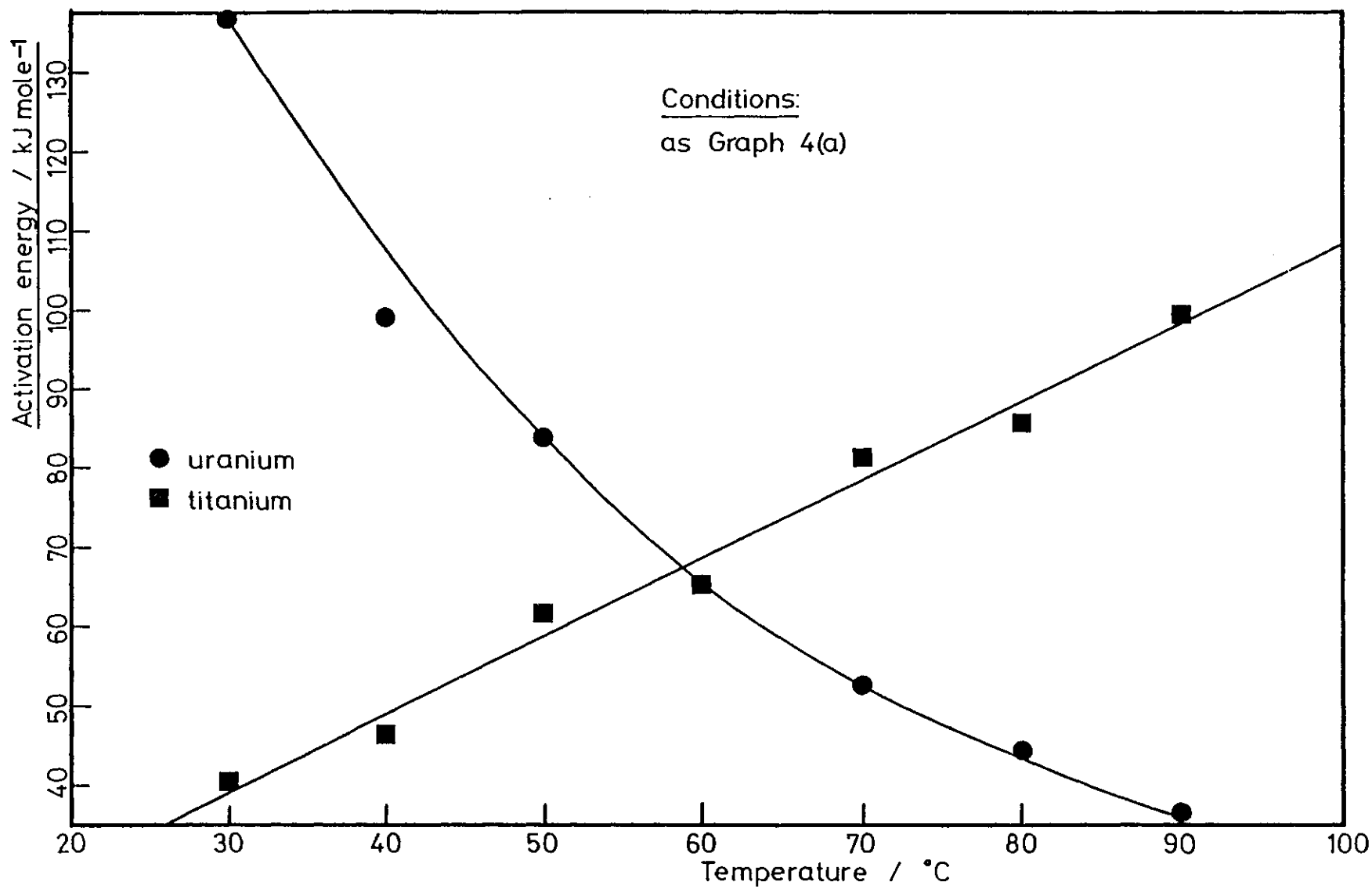
Graph 4(b) As Graph 4(a) Titanium extraction



Graph 4(c) As Graph 4(a) Rate of uranium extraction, as a function of temperature,
after 5% extraction



Graph 4(d) As Graph 4(a) Rate of titanium extraction, as a function of temperature,
after 5% extraction



Graph 4(e) Activation energies for U and Ti dissolution, as a function of temperature, after 5% extraction

function of time, have similar characteristics of progressively decreasing rates of dissolution. Not surprisingly, rates of leaching and overall dissolutions increased with temperature in both cases.

Table 13(b) shows that the Ti:U mole ratios of dissolution were similar to those of previous experiments, in that uranium was preferentially soluble in the early stages of dissolution. As leaching proceeded, the stoichiometric situation was approached, although, for the lower temperature leaches, the equilibrium regime was far from being established, even after 30 hours of leaching.

The data do not fit the shrinking core models. Correlation of the uranium dissolution data is again shown with the mixed kinetic control model. At the higher temperatures the model fits over the whole range of time, but at lower temperatures only the later-time data can be fitted with any confidence. Fitting of this model is discussed later. The titanium results do not fit the model at any temperature.

Activation energies for the dissolution processes of uranium and titanium were calculated from the data obtained in the leaching studies. An Arrhenius relationship for a reaction can be written

$$\text{Rate} \propto A \cdot e^{-E_a/RT} \quad (2)$$

where A = constant

E_a = activation energy

R = gas constant

T = absolute temperature.

Re-writing gives:

$$\ln (\text{Rate}) = C - \frac{E_a}{R} \cdot \frac{1}{T} \quad (3)$$

where C = constant.

Plotting $\ln(\text{Rate}) \text{ v } \frac{1}{T}$ will give a line, with slope equal to $-\frac{E_a}{R}$, from which the activation energy can be calculated.

The problem in a dissolution study is choosing the point at which a "rate" should be measured. There is little justification in taking the rate at the start of a leach run and assuming it to be linear between time = 0 and (say) time = $\frac{1}{2}$ hour. The initial rate can be influenced by many factors, many of which are unrepresentative of the true leaching process. Such factors might include, amongst others, fine dust-like particles on the surface, or especially active sites resulting from sample preparation.

A more representative "rate" is one measured when the leaching regime is well established. For this reason, it was decided to measure the rates of dissolution after 5% metal extraction, for both U and Ti leaching. At this stage, a settled regime was underway with dissolution approaching a stoichiometric path, as discussed for prior experiments.

From Graph 4(b), it can be seen that the total titanium extraction did not reach 5% at the lower leaching temperatures. However, in these cases the extraction of Ti was linear with time and it was assumed to remain so up to 5%, giving a constant rate.

Rates at 5% dissolution were found from the U and Ti leaching curves and plotted in the Arrhenius fashion of $\ln(\text{Rate})$ as a function of $(\text{absolute temperature})^{-1}$.

Graph 4(c) shows the Arrhenius plot for uranium extraction. The plot is obviously a curve, with increasing (negative) slope on decreasing temperature. From equation (3), a curved line and hence, changing slope with temperature, indicates a varying activation energy with temperature. This is indicative of a process in which the mechanism of reaction is temperature-dependent. The

slope of the Arrhenius plot was evaluated at 10°C intervals between 30°C and 90°C and the corresponding E_a values calculated from equation (3). The E_a values are shown in Table 13(c). They are also plotted, as a function of temperature, in Graph 4(e). From this plot, it can be seen that the E_a values varied from $\sim 137 \text{ kJ mole}^{-1}$ at 30°C to $\sim 36 \text{ kJ mole}^{-1}$ at 90°C.

In hydrometallurgical processes, the mechanism of kinetic control can usually be characterised by the activation energy and, as a general rule of thumb, the following relationships hold:

$E_a = 16\text{--}20 \text{ kJ mole}^{-1}$ - diffusional control

$E_a = 20\text{--}60 \text{ kJ mole}^{-1}$ - mixed diffusional and chemical control, with diffusional control predominating at low E_a values and vice versa.

$E_a > 60 \text{ kJ mole}^{-1}$ - chemical control

From the results obtained in the current work, it would appear that the dissolution of uranium at lower temperatures was under total chemical control and significant diffusional control only began to operate at temperatures in excess of $\sim 60^\circ\text{C}$. Further increases in temperature indicated an increasing importance of the diffusional control factor, as might be expected.

Clearly, under normal atmospheric leaching conditions, total diffusional control of uranium dissolution was not achieved. This can be cited as one of the reasons for the non-applicability of the shrinking-core models of leaching. These assume a diffusion-controlled regime. However, the activation energy at 75°C ($\sim 47 \text{ kJ mole}^{-1}$) confirmed the observations of previous experiments that uranium extraction data fit the mixed kinetic control model, within experimental error. The mixed control model was developed on the basis that the leaching rate

was controlled by two factors, namely diffusional processes and surface chemical reactions. This seems to be an accurate reflection of the kinetic control of leaching, as indicated by the observed E_a values. Further, the model assumes the formation of products on the surface through which diffusion occurs. The previous observations of the change in Ti:U ratio, approaching the stoichiometric value of 2.0, and the proposed mechanism by which this occurred are also in agreement with the model.

A similar evaluation procedure was undertaken using the titanium dissolution data. The Arrhenius plot and (E_a as a function of temperature) plot are given in Graphs 4(d) and 4(e), respectively. The Ti-Arrhenius plot shows different characteristics to the corresponding U plot in that the (negative) slope of the line increases with temperature and hence, from equation (3), there was an increase in E_a with temperature during leaching, as shown in Graph 4(e). Again, the Arrhenius plot is curved indicating a temperature dependent mechanism. The E_a results of $\sim 40 \text{ kJ mole}^{-1}$ at 30°C rising to $\sim 100 \text{ kJ mole}^{-1}$ at 90°C show an approximately linear dependence on temperature. At the lower end of the temperature scale, mixed kinetics appear to have prevailed whilst above $\sim 50^\circ\text{C}$, the mechanism of dissolution was apparently under total chemical control.

An increase in activation energy with temperature seems to be a very strange phenomenon, but it might be explained in terms of the mode of dissolution on a microscopic scale. It can be envisaged that uranium was preferentially soluble and the kinetics of solubility were increased on increasing the temperature. As uranium was removed, left behind was a Ti/oxide lattice of increasing disorder, caused by disruption on U removal. The destruction of the ordered brannerite lattice hindered the dissolution

of Ti, creating a kinetic barrier. On increasing temperature, the sequence of events might be summarised:-
 increasing temperature → increasing uranium dissolution kinetics → increasing rate of disordering of lattice
 → increasing rate of hindrance to titanium dissolution
 → increasing kinetic barrier to titanium dissolution
 → increasing activation energy for titanium leaching.
 These observations would explain why the Ti data do not fit the mixed control model for leaching; at high temperatures, dissolution was by a chemically controlled mechanism and at lower temperatures, a uniform leaching regime was unlikely to have been reached. However, the above model, proposing the formation of a "product" layer (of Ti-rich, disordered lattice), is consistent with the mixed model for uranium dissolution.

3.2.1.1.(v) Effect of particle size

The effects of particle size on leaching pure brannerite in 100 g/l H_2SO_4 , at 75°C , with 10 g/l Fe^{3+} present as an oxidant, were investigated. Clearly, the crushed brannerite powders had a range of sizes, so experiments were performed on sieve fractions with a limited particle size range.

Surface area measurements were carried out on the bulk sieve fractions, prior to leaching. However, only 1 gramme samples of material were leached and the resulting residues were too small to obtain any sensible surface area measurements. Surface area measurements can be summarised as:

Sieve fraction (microns)	specific surface area/cm ² gm ⁻¹
-180 + 125	insufficient sample
-125 + 90	320.08
- 90 + 63	403.41
- 63 + 53	478.09
- 53 + 45	512.01
-38	551.86

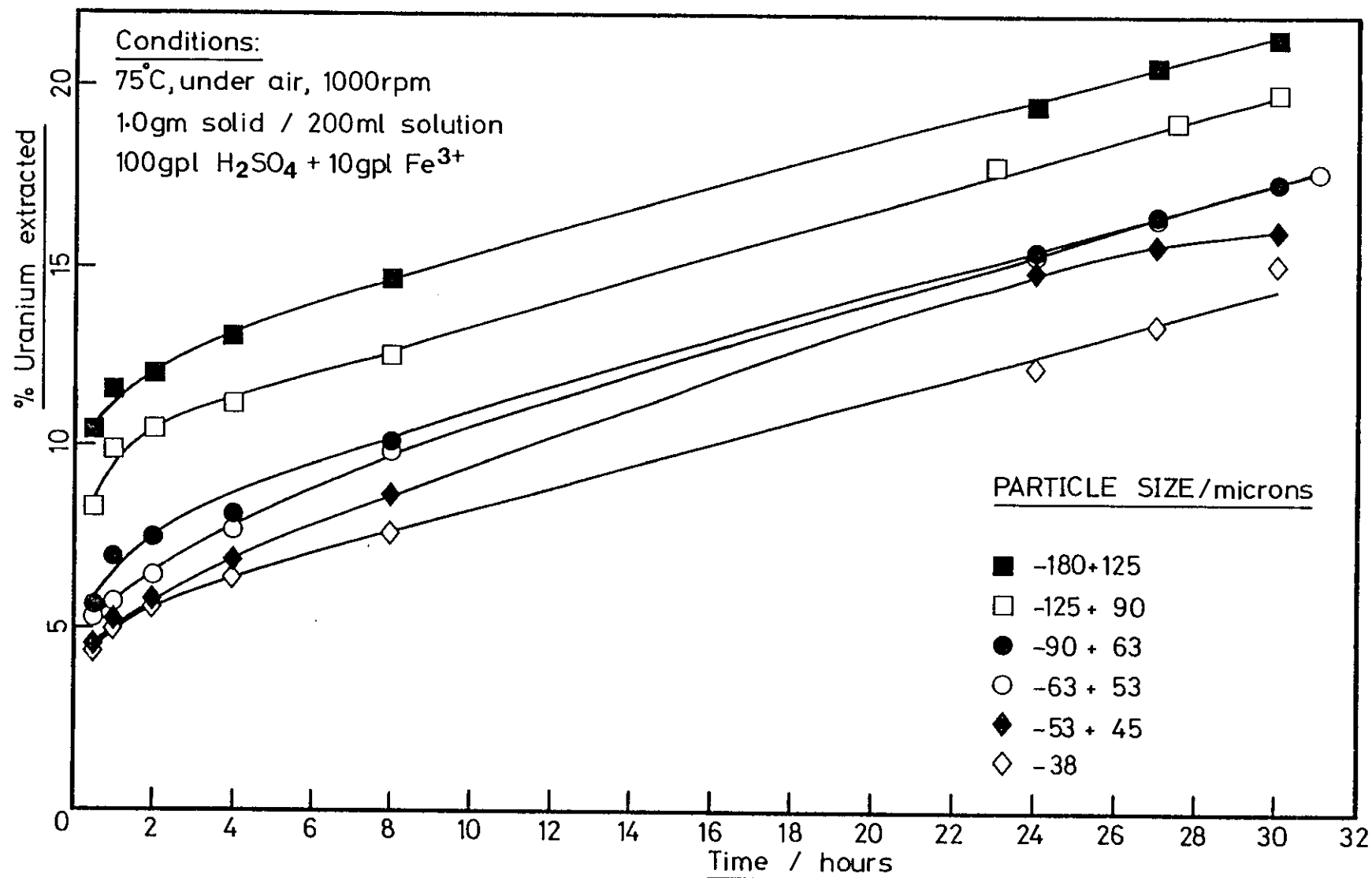
As expected, the specific surface areas of the powders increased as the particle sizes decreased.

Results: Table 14, Graph 5.

The graph shows that the uranium leaching rates were, soon after the start, virtually independent of particle size. This was very surprising since it might reasonably have been expected that reduction in particle size, and hence, increase in surface area, would have brought about increased dissolution kinetics. Furthermore, it would appear that, as the particle size was decreased, the overall uranium extraction was decreased. The titanium dissolution results (not shown) exhibited similar characteristics and the Ti:U ratios indicated initial U solubility, followed by the usual tendency towards stoichiometric leaching.

The results were contrary to experience and two possible explanations were examined. It was first thought that uranium in solution might have been adsorbed onto an active mineral surface; the higher available surface areas of the smaller particles would have provided a means of explaining the anomalous results. However, a controlled series of agitation tests of mineral in artificial leach liquors, of known uranium contents, showed there to be negligible adsorption of uranium from solution, as might be expected in such strongly acidic conditions. Experience has shown that U adsorption is only really a problem in alkali leaching.

The alternative explanation was that the mineral had undergone some structural changes right at the start of the leaching runs. Plate 8 shows particles of pure brannerite, of $-125 + 90$ micron sieve size, prior to leaching. Although the particles are regularly shaped, they are exceedingly porous. The nature of the particles is consistent with breaking up the "pumice-stone" network of the brannerite sinter block, described previously.



Graph 5 Effect of particle size on leaching pure brannerite in 100gpl H_2SO_4 containing 10gpl Fe^{3+}

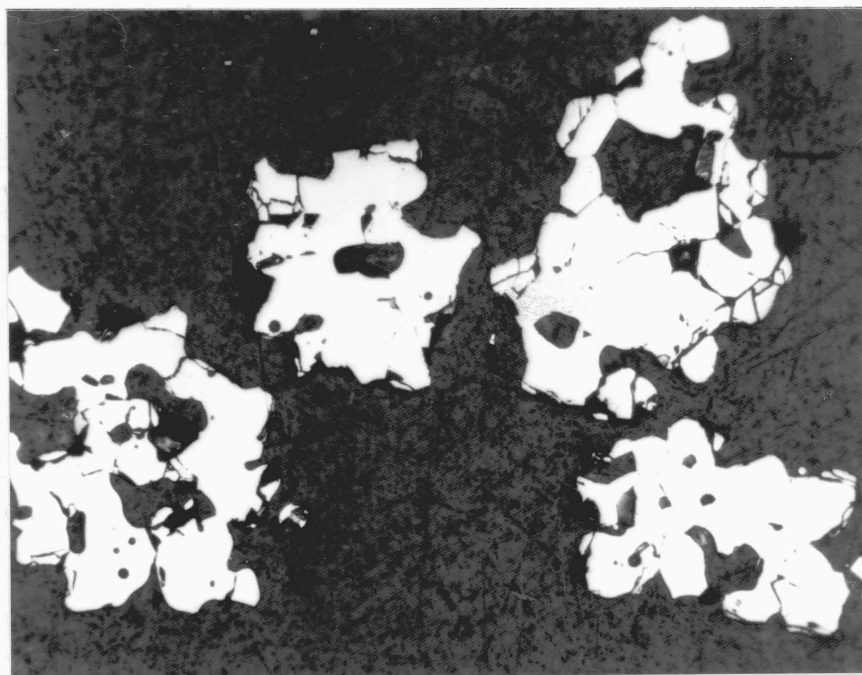


Plate 8, Pure brannerite, -125 + 90 microns, particles prior to leaching.

x300. Particles are regularly shaped but porous, having a "network" appearance.

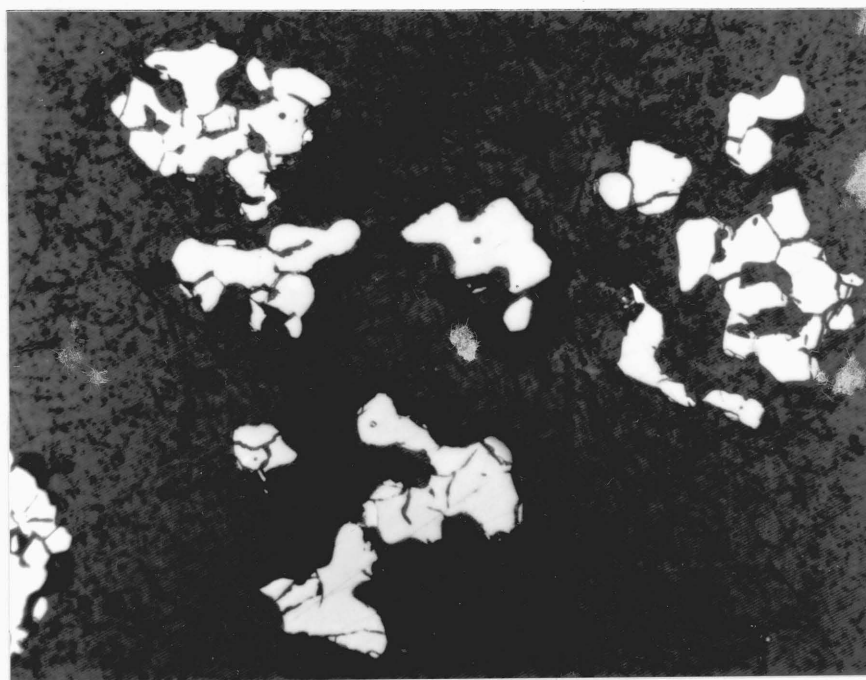


Plate 9, Pure brannerite, -125 + 90 microns, leach residue.
x300. Leaching conditions: 100 g/l H_2SO_4 , 10 g/l Fe^{3+} , 75°C, 30 hours, 20% U, 20% Ti removal. Shows fragmentation of particles on leaching.

The particles show areas which are fairly solid, but the connections between the solid areas are less bulky and these "bridging-sites" enclose the pores.

Plate 9 shows the above sinter after leaching for 30 hours, under the conditions described earlier, resulting in ~20% U (and ~20% Ti) extraction. Clearly, a considerable breakdown is evident, resulting in fragmentation of the particles. There is less evidence of internal porosity, with the residue consisting of "solid" particles. A process appears to have occurred by which the "bridging-sites" were preferentially dissolved to liberate the solid volumes of brannerite. The preferential dissolution of the "bridging-sites" is consistent with a pitting-type of attack, although this was not investigated further. The activation energy values (determined previously) are also such that an electrochemical attack, of this nature, cannot be ruled out.

The size of the residue particles and the relatively low extractions of U and Ti discounted the possibility that the attack had been uniform throughout the course of leaching, with fragmentation occurring by progressive dissolution of the thinner "bridging-sites". It is estimated that, for this mode of leaching, extractions of the order of 50% would have been necessary to produce the observed results.

It is envisaged that preferential dissolution, at the "bridging-sites", occurred very rapidly at the start of leaching, producing a residue of approximately the same size and surface area for all the initial starting conditions. This would explain the uniform rate of uranium extraction experienced in later stages. The bigger particle sizes, initially having more "bridging-sites" and, therefore, preferred dissolution sites, resulted in large initial metal leaching rates and hence overall extraction, as shown.

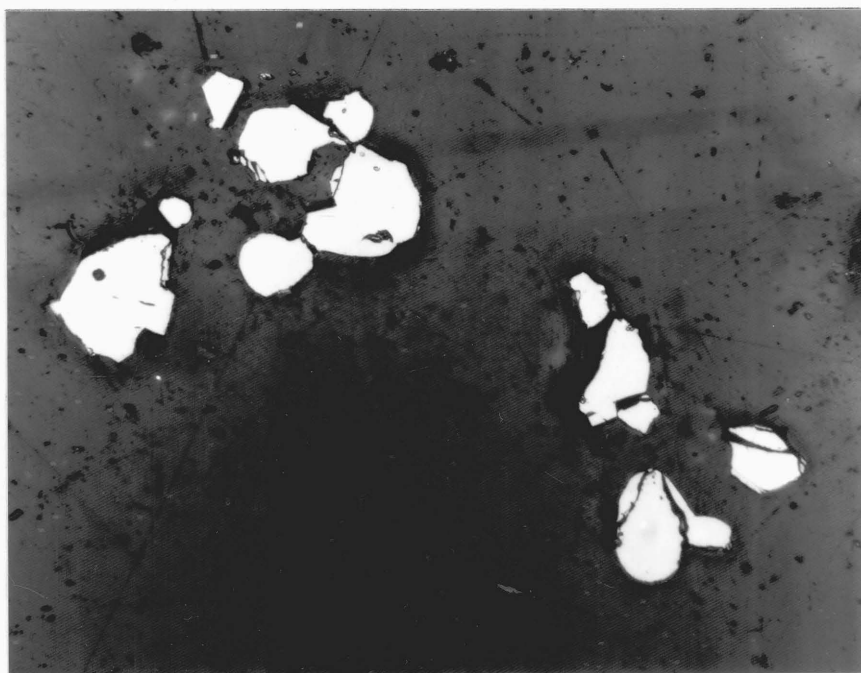


Plate 10, Pure brannerite; -53 + 45 microns, particles prior to leaching.

x300. Regular particles showing little internal porosity. The particles were probably formed from breaking up networks of bigger particles.

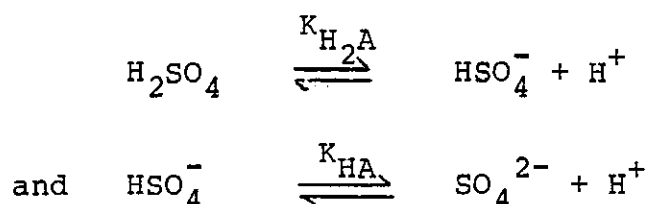
Plate 10 shows particles of pure brannerite of -53 + 45 micron size, prior to leaching, for comparison with Plate 8. The particles are regular, solid, exhibit little internal porosity and, therefore, contain few "bridging-sites". The particles appear to have been formed on breaking-up the network of the sinter block. In terms of the mechanism proposed above, such particles have few preferred leaching sites, so reducing the initial metal extraction as indicated by the experimental data.

As before, only the uranium data fit the mixed kinetic model with any degree of correlation.

3.2.1.1.(vi) Effect of leaching in various inorganic acids

The effects of leaching pure brannerite in sulphuric, nitric and hydrochloric acids were compared at 75°C, in the absence of an oxidant. For convenience, a H_2SO_4 concentration of 1 molar was chosen, but a problem arose in choosing HCl and HNO_3 of "equivalent leaching power".

The dissociation of H_2SO_4 is virtually complete at concentrations below 11 M. The species present are then determined by the equilibria:



At sufficiently high pH values, the bisulphate ions are almost totally dissociated and sulphate ions are the sole ionic species. At sufficiently low pH values, the bisulphate ions will be the major anion species. However, at the pH under consideration, the bisulphate ion concentration could not be readily determined by experiment and evaluation of K_{HA} and $K_{\text{H}_2\text{A}}$ requires a considerable amount of guess/estimation⁽⁵⁶⁾ work on data which vary considerably in the literature⁽⁵⁶⁾. Thus, a simplified approach to leaching, with acids of "equivalent leaching power", was undertaken.

In acid leaching, the leaching agent might be considered to be the hydrated proton, H_3O^+ . In one molar H_2SO_4 , the two extremes of dissociation would give, if possible:

$\text{H}^+ = 2 \text{ M}$ for dissociation to sulphate ions only
 and $\text{H}^+ = 1 \text{ M}$ for dissociation to bisulphate ions only.
 In reality, the H^+ concentration will lie between the two. Similarly, a 0.5 M H_2SO_4 solution will have, at the extremes, $\text{H}^+ = 1 \text{ M}$ and 0.5 M respectively, with the real value lying between.

Hence, two H_2SO_4 leaches were undertaken with acid concentrations of 0.5 M and 1.0 M. It was assumed that a leach with $\text{H}^+ = 1.0 \text{ M}$ would show characteristics between the two extremes. For comparison, equivalent HCl and HNO_3 solutions were prepared such that, on titration, the H^+ concentrations were exactly 1.0 M.

Results: Table 15, Graphs 6(a),(b).

It can be seen that brannerite showed no significant leaching in any of the acids, in the absence of an oxidant. Uranium and titanium solubility followed similar curves. There was no real difference between leaching in HCl and H_2SO_4 , but there was a marginal improvement with HNO_3 , although after 10 hours only 2.5% U and 1% Ti had been extracted.

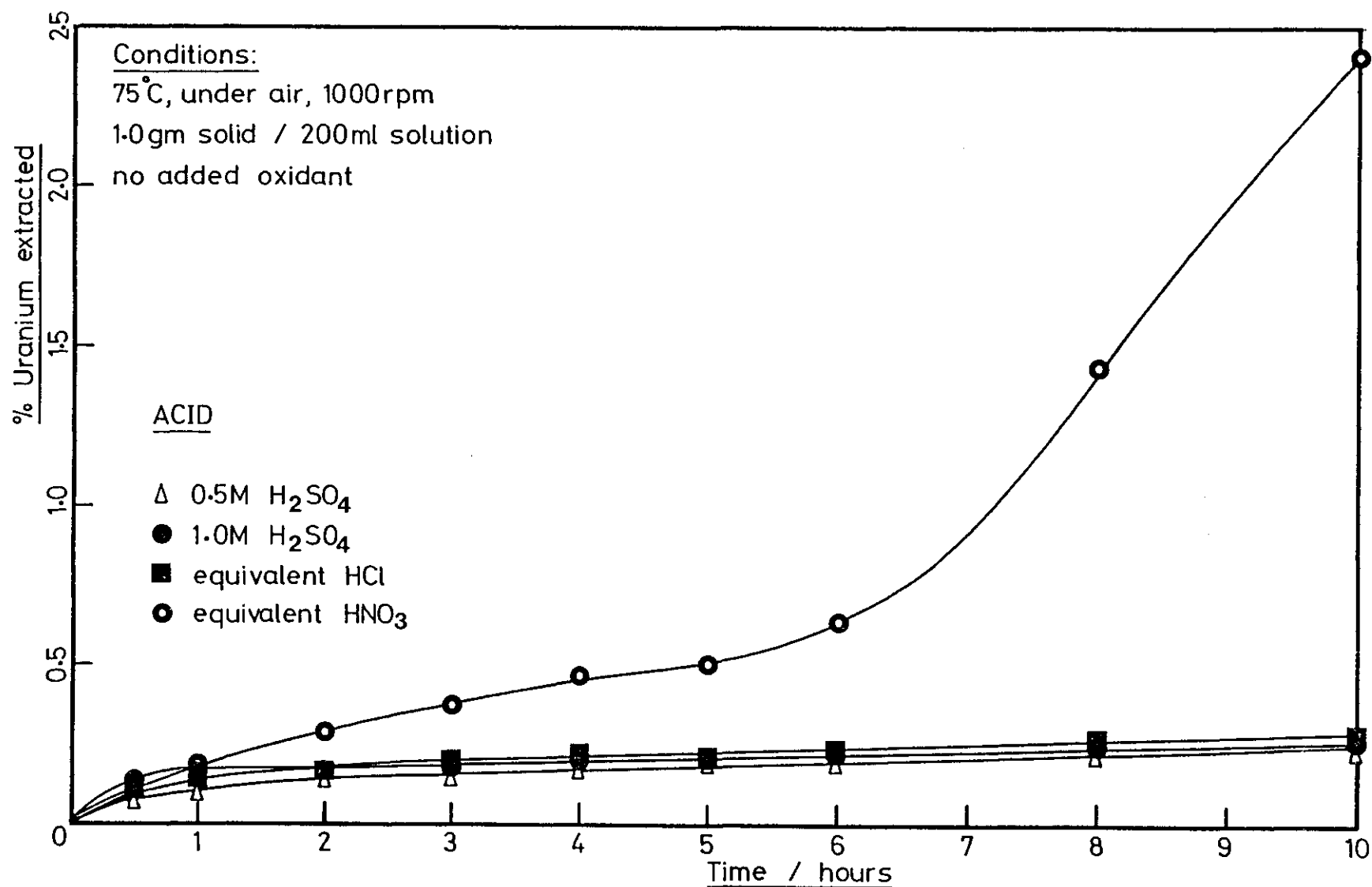
The Ti:U ratios show that uranium was extracted preferentially.

The data do not fit any of the leaching models, as expected, since no steady-state leaching regime had been achieved. Clearly, leaching brannerite in H_2SO_4 , HCl and HNO_3 showed it to be virtually resistant to attack, in the absence of an oxidant.

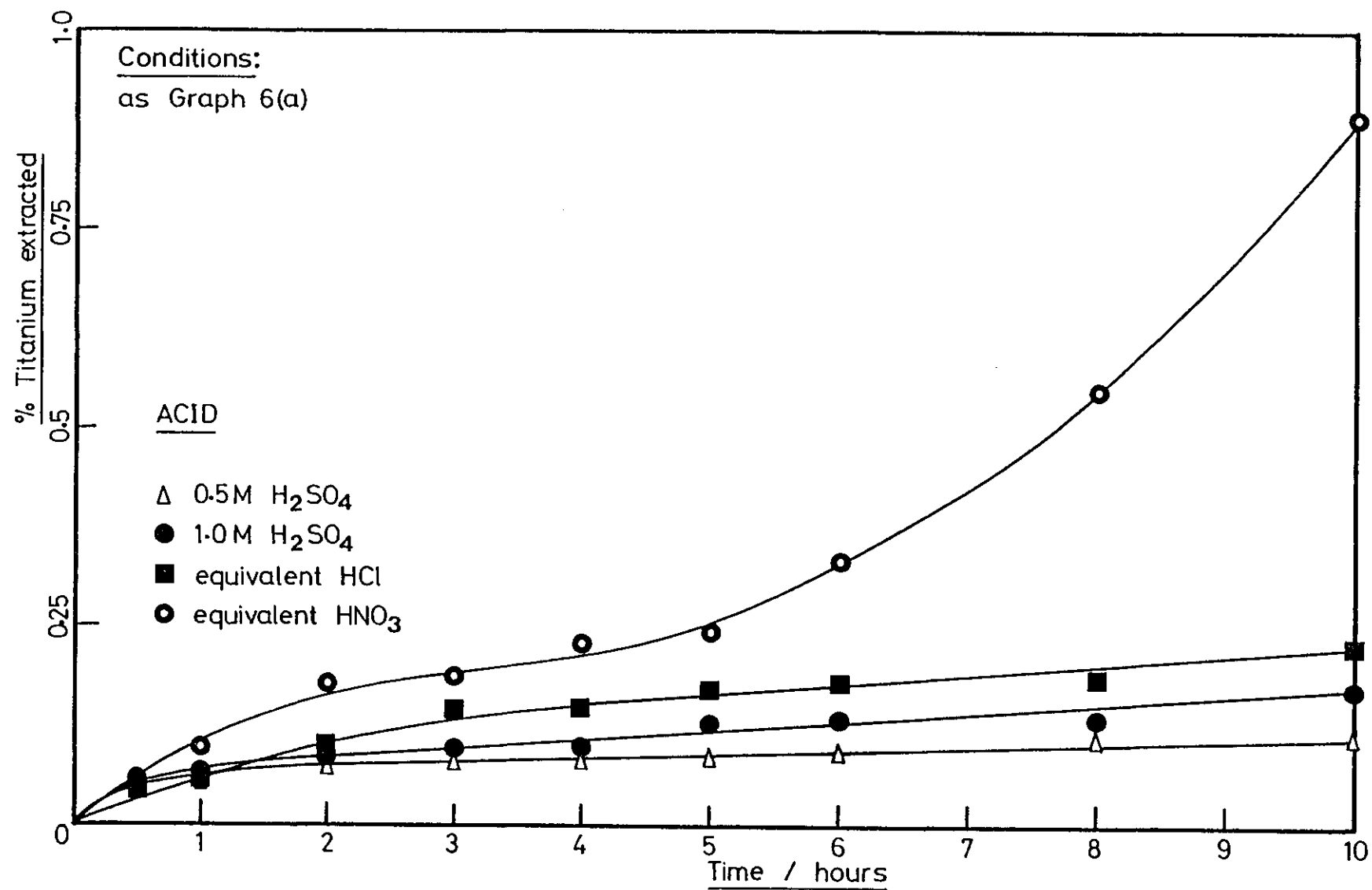
3.2.1.1.(vii) Effect of leaching in various inorganic acids containing an oxidant

A series of leaching tests was carried out to investigate the leaching of pure brannerite in H_2SO_4 , HCl and HNO_3 of "equivalent leaching power" (as described in the previous section), in the presence of an oxidant, at 75°C . The oxidant chosen was the ferric ion at a concentration of 10 g/l. The oxidant was added as the ferric sulphate, chloride and nitrate respectively, and it was assumed that all the iron was in the trivalent state.

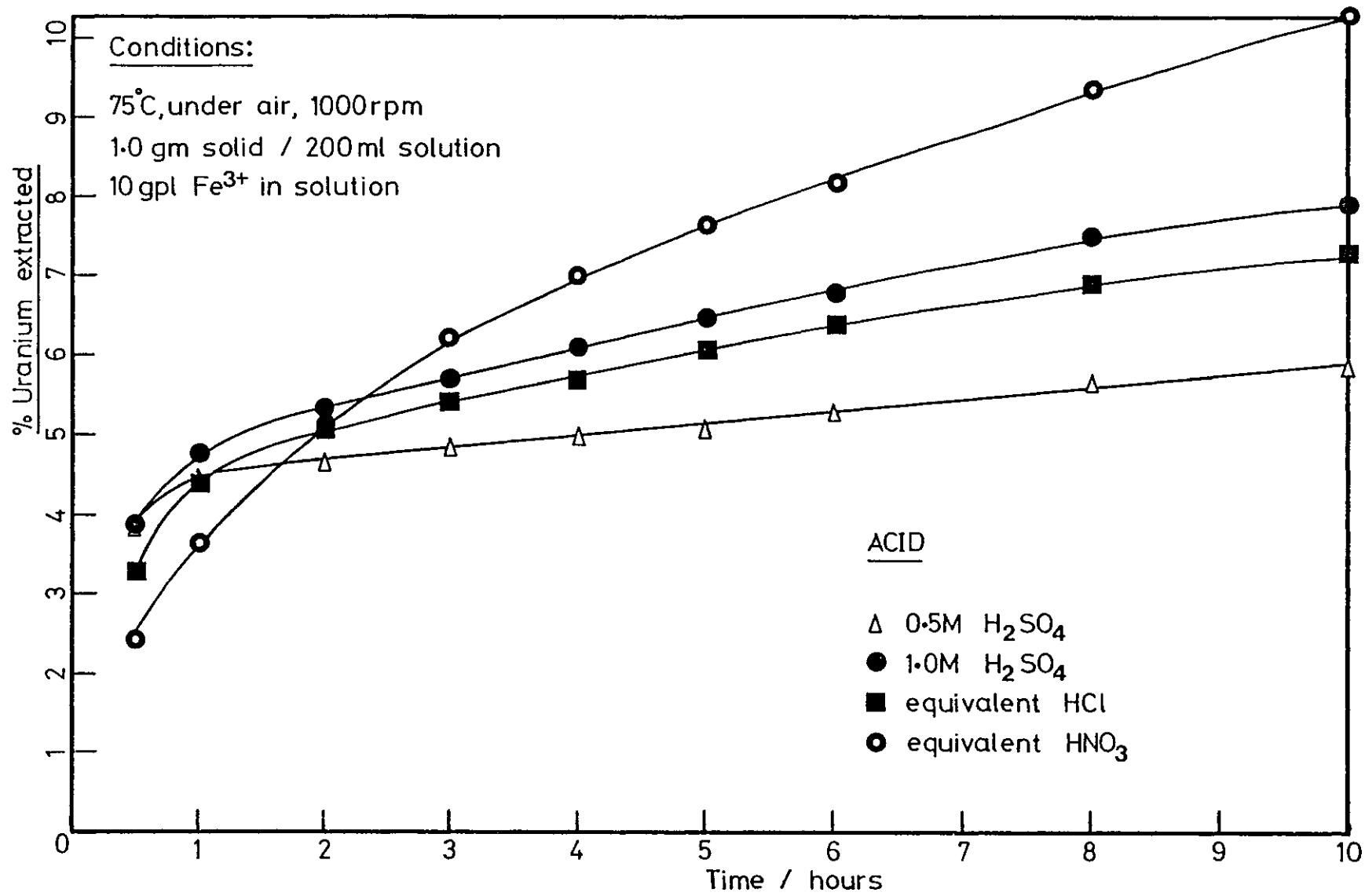
Results: Table 16, Graphs 7(a),(b),(c).



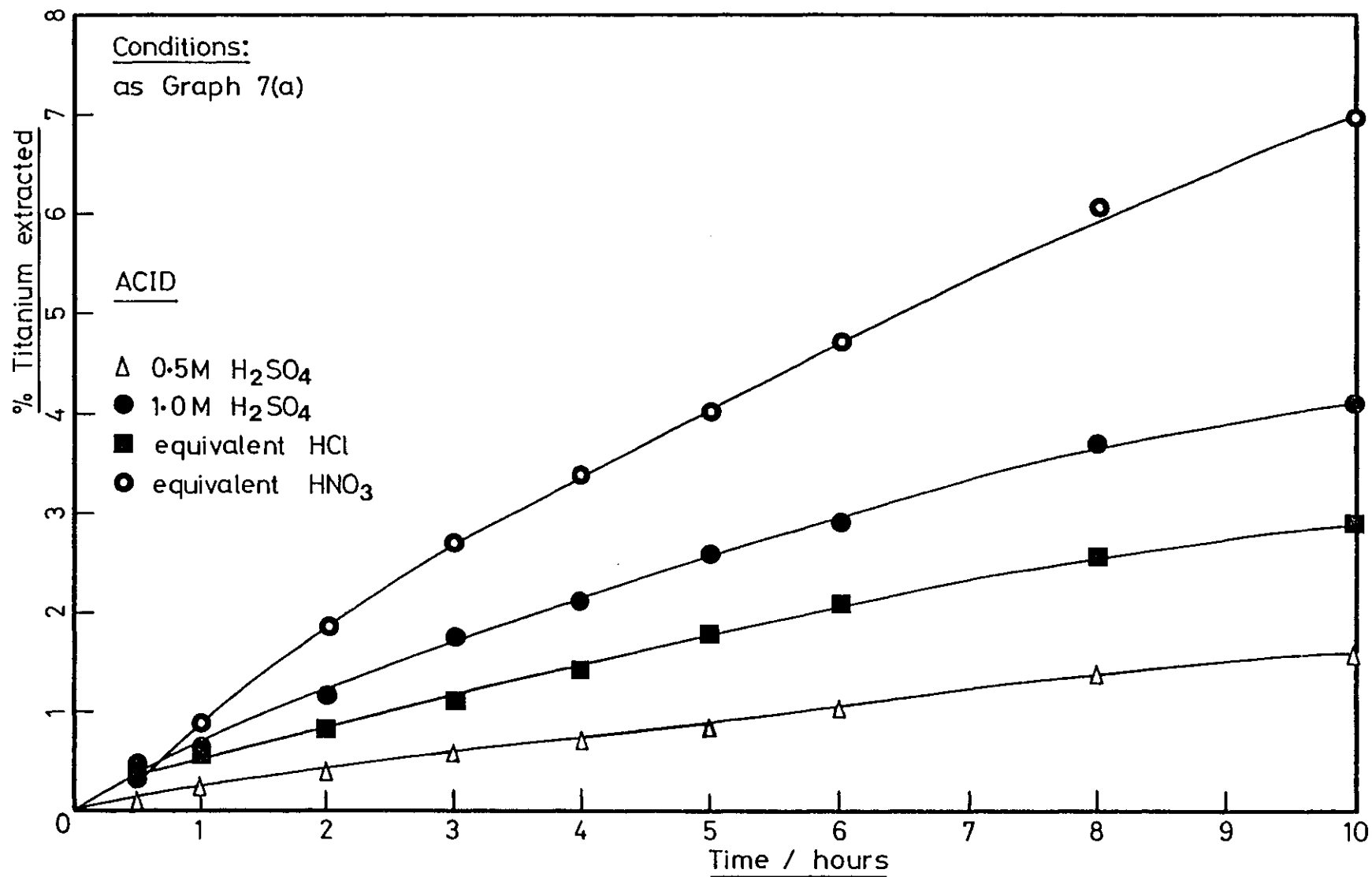
Graph 6(a) Effect of leaching pure brannerite in inorganic acids of molarity equivalent to 1M H₂SO₄:- uranium extraction



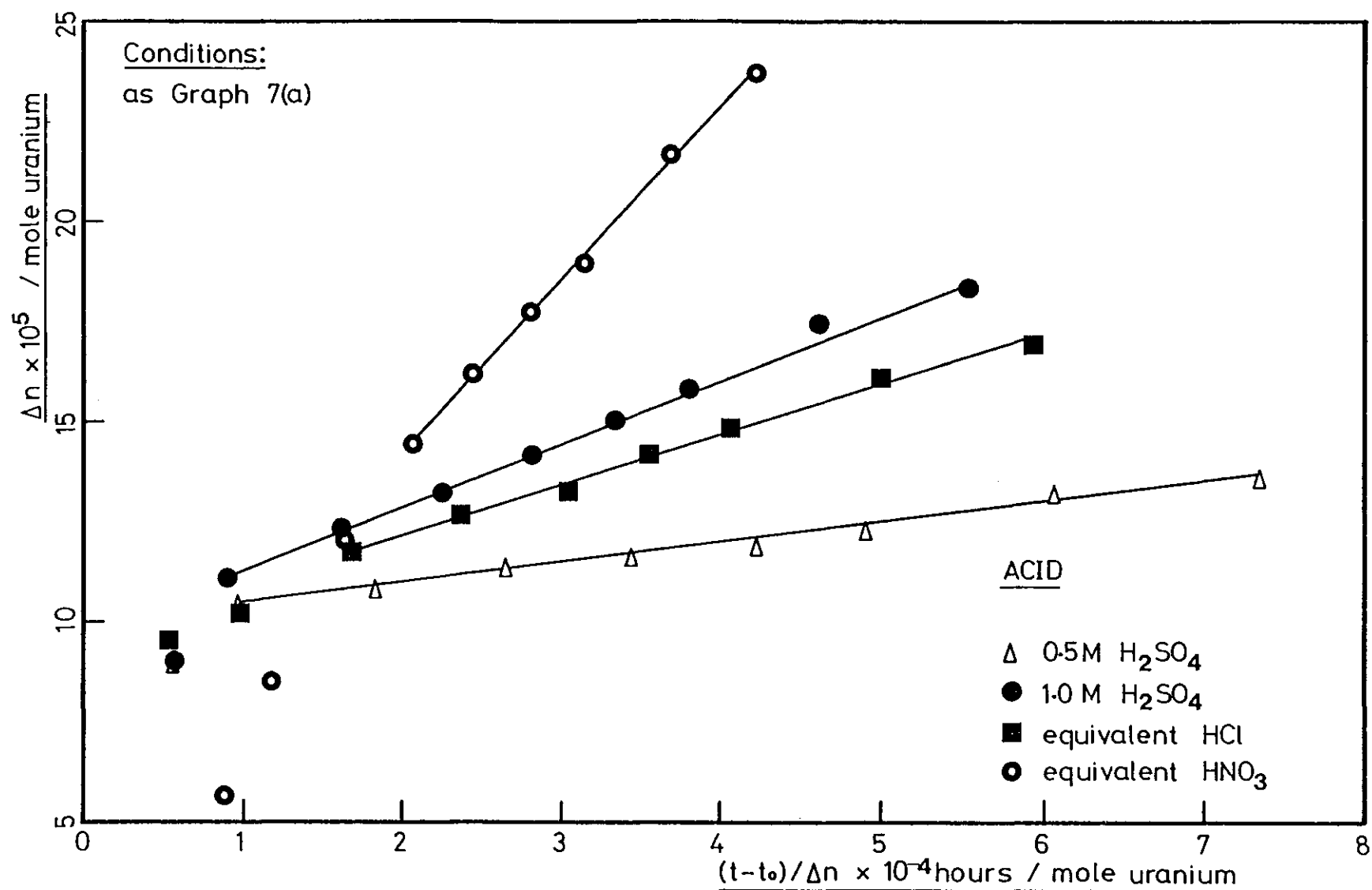
Graph 6(b) As Graph 6(a) Titanium extraction



Graph 7(a) Effect of leaching pure brannerite in ferric iron-containing inorganic acids of molarity equivalent to 1M H_2SO_4 — uranium extraction



Graph 7(b) As Graph 7(a) Titanium extraction



Graph 7(c) As Graph 7(a) Plot to confirm applicability of mixed kinetic control model,
 Δn v. $(t-t_0)/\Delta n$

As might have been expected, the presence of an oxidant had facilitated the leaching of brannerite. The dissolution curves for U and Ti show roughly similar characteristics of progressively decreasing rates. The positions of the HCl plots on Graphs 7(a) and 7(b) indicate that HCl and H_2SO_4 (+ equal oxidant) had similar abilities to leach brannerite.

Nitric acid (+ oxidant), although showing a marginally lower initial metal removal, exhibited a higher leaching rate throughout the course of leaching, with the consequent higher overall dissolution. It is probable that this result arose due to the exceptionally stable nature of the uranyl nitrate complex. However, the increase in uranium dissolution (over H_2SO_4 and HCl leaching) is hardly sufficient to warrant the use of nitric acid on a commercial scale. H_2SO_4 would appear to be a perfectly adequate leaching medium, in view of the considerations outlined in the literature survey, with respect to the other acids.

The Ti:U ratios show uranium to have been preferentially soluble in all three media; all the ratios increased with time and metal extraction towards the stoichiometric value of 2.0.

As anticipated, none of the data fit the shrinking core models and the Ti data do not fit the mixed kinetics model. Graph 7(c) shows the uranium data plotted in terms of the mixed kinetic control model. The correlation is excellent, except in the early stages of leaching, confirming mixed chemical and diffusional control. It can be concluded that the modes of dissolution in all three inorganic acids, H_2SO_4 , HCl and HNO_3 , had similar characteristics.

3.2.1.1.(viii) Effect of sulphuric acid concentration with constant oxidant level

The effects of leaching pure brannerite in 0.5, 1.0 and 2.0 M H_2SO_4 , containing a constant oxidant level of 10 g/l Fe^{3+} , were studied at 75°C.

Results: Table 17, Graphs 8(a), (b), (c).

The uranium and titanium dissolution curves show similar characteristics of progressively decreasing rates with time. The effect of acid concentration on the rates was as expected:

$$2.0 \text{ M} > 1.0 \text{ M} > 0.5 \text{ M},$$

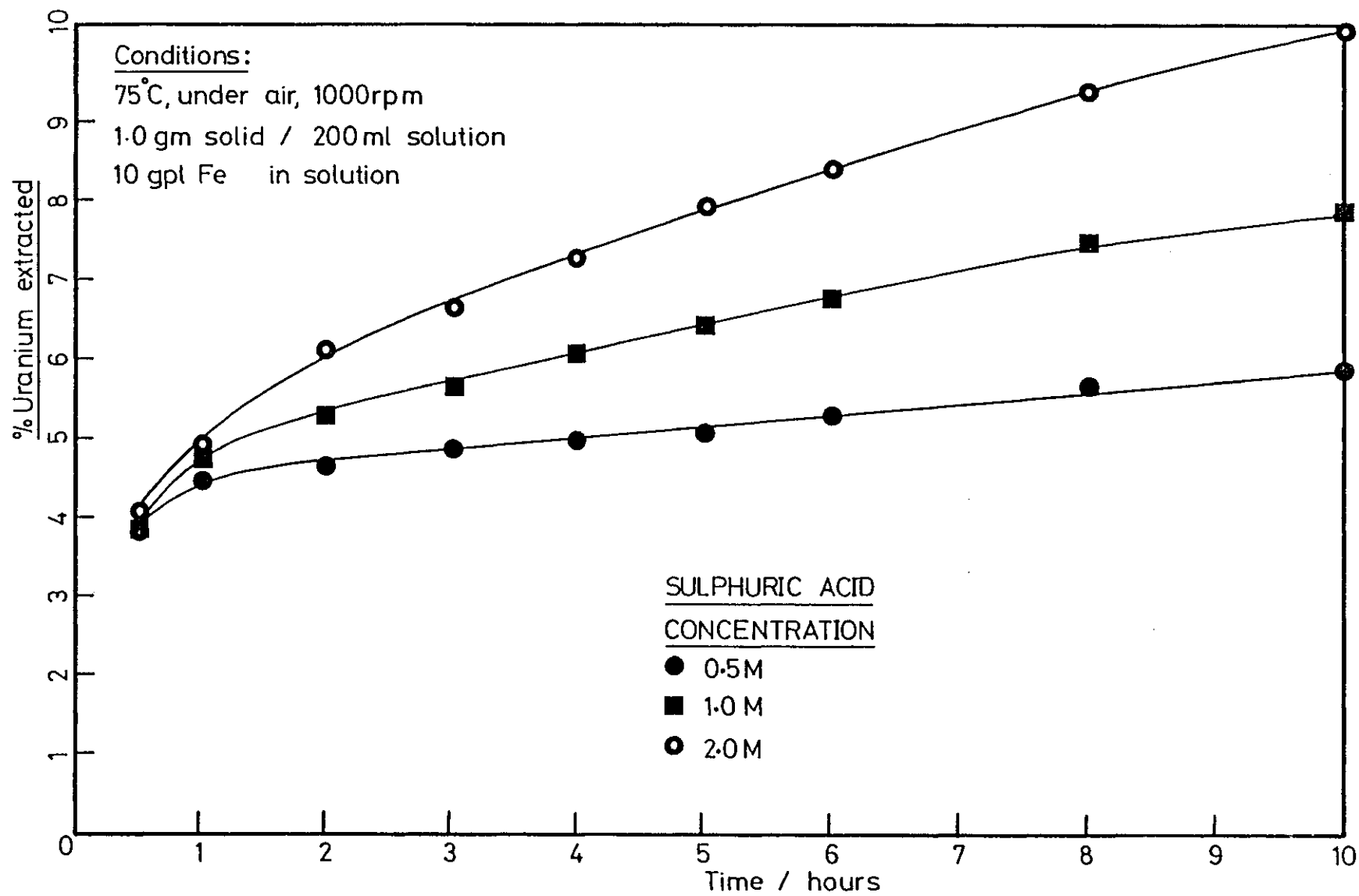
although there seemed to be no simple relationship between doubling acid concentration and metal dissolved.

The Ti:U ratios show that U was preferentially dissolved in all cases, but the ratios increased with time and metal extraction towards the stoichiometric value, agreeing with earlier observations and discussion.

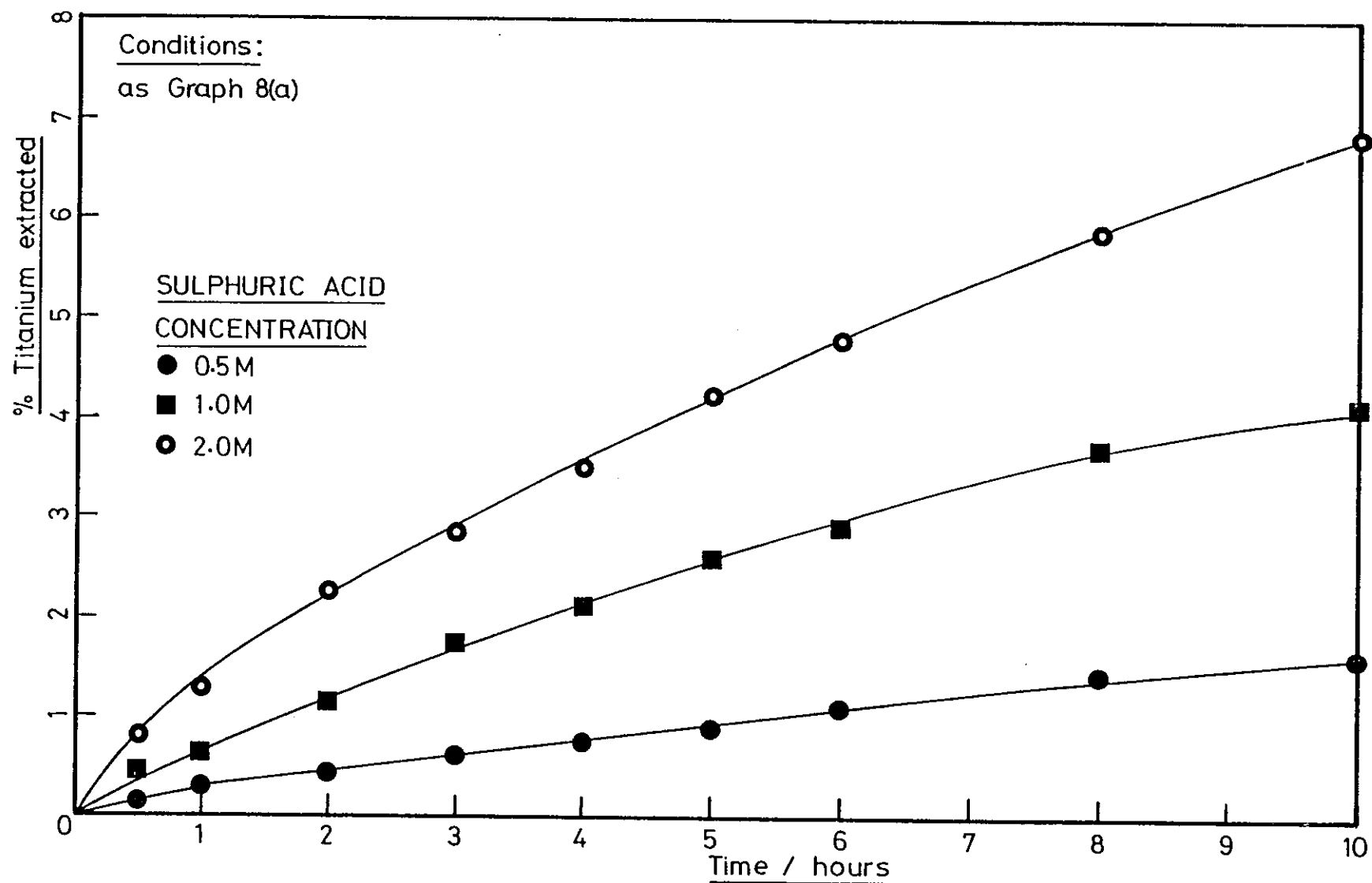
As before, the Ti data fit none of the leaching models. The uranium dissolution data again fit the model for mixed kinetic control of leaching. The data are plotted in Graph 8(c). Log (extraction) vs log (time) plots indicated complex reaction mechanisms.

3.2.1.1.(ix) Potential and pH changes on leaching

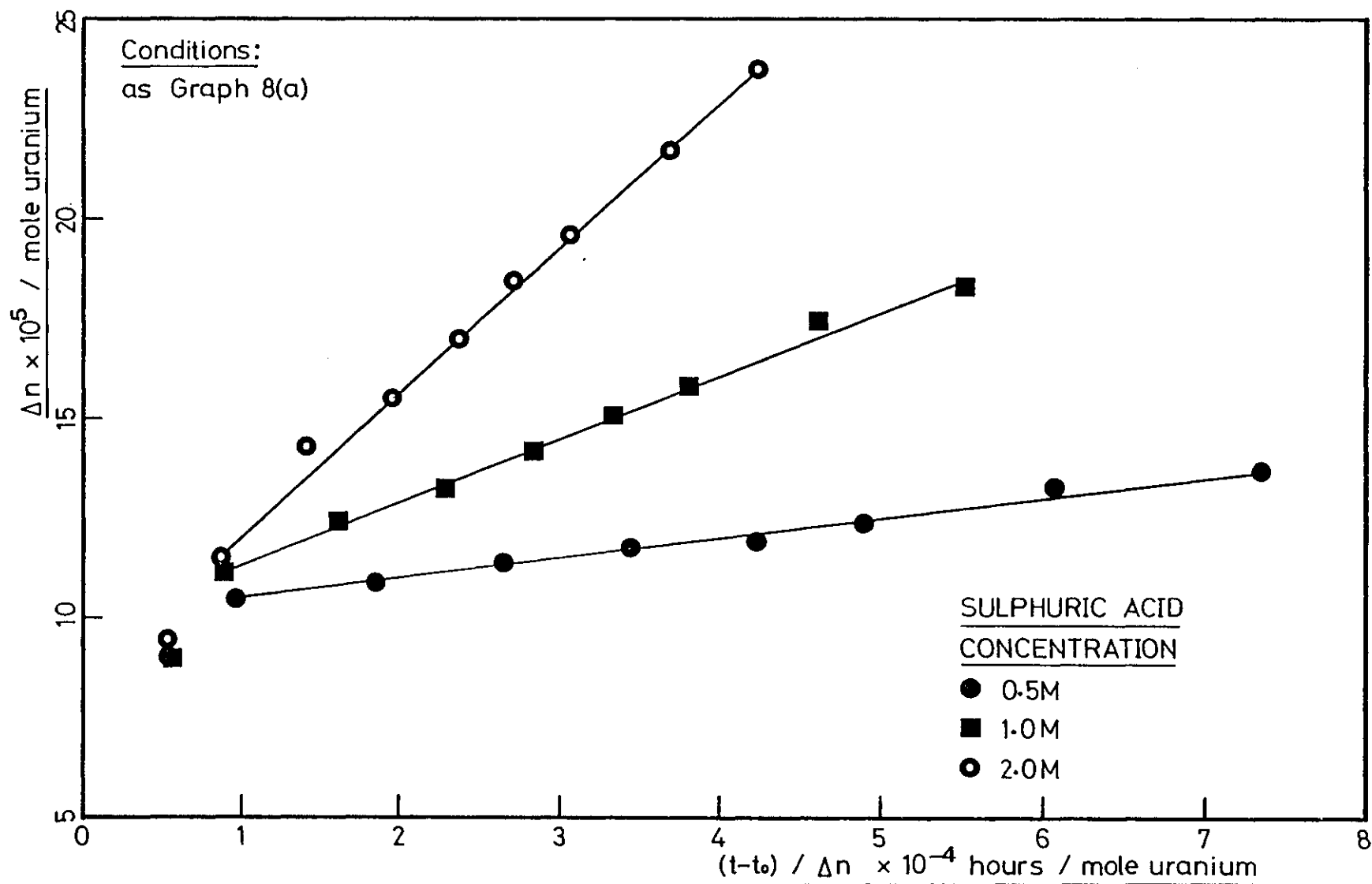
An attempt was made to monitor the oxidation potential and pH changes during the course of selected runs. However, brannerite required such strongly oxidising, acidic conditions to liberate any U (and Ti) that the exercise was rendered impracticable:



Graph 8(a) Effect of leaching pure brannerite in sulphuric acid of varying concentration
with constant oxidant level, 10gpl Fe³⁺ :- uranium extraction



Graph 8(b) As Graph 8(a) Titanium extraction



Graph 8(c) As Graph 8(a) Plot to confirm applicability of mixed kinetic control model,
 $\Delta n \text{ v. } (t-t_0) / \Delta n$

- the acid solutions gave pH measurements in the region of zero and measurements of pH and changes in pH were too inaccurate to be useful.
- solutions containing 10 g/l Fe^{3+} , as an oxidant, showed very high oxidation potentials of ~ 1150 mV. On addition of the solid to the leach liquor, it was found that the potential dropped by between 60 and 70 mV, but during the course of the leach run the E_H decreased by only a further 15-20 mV, even after 30 hours leaching. Such a decrease was considered insignificant in view of the overall potential and it was concluded that, during the experiments, leaching was performed under strongly oxidising conditions.

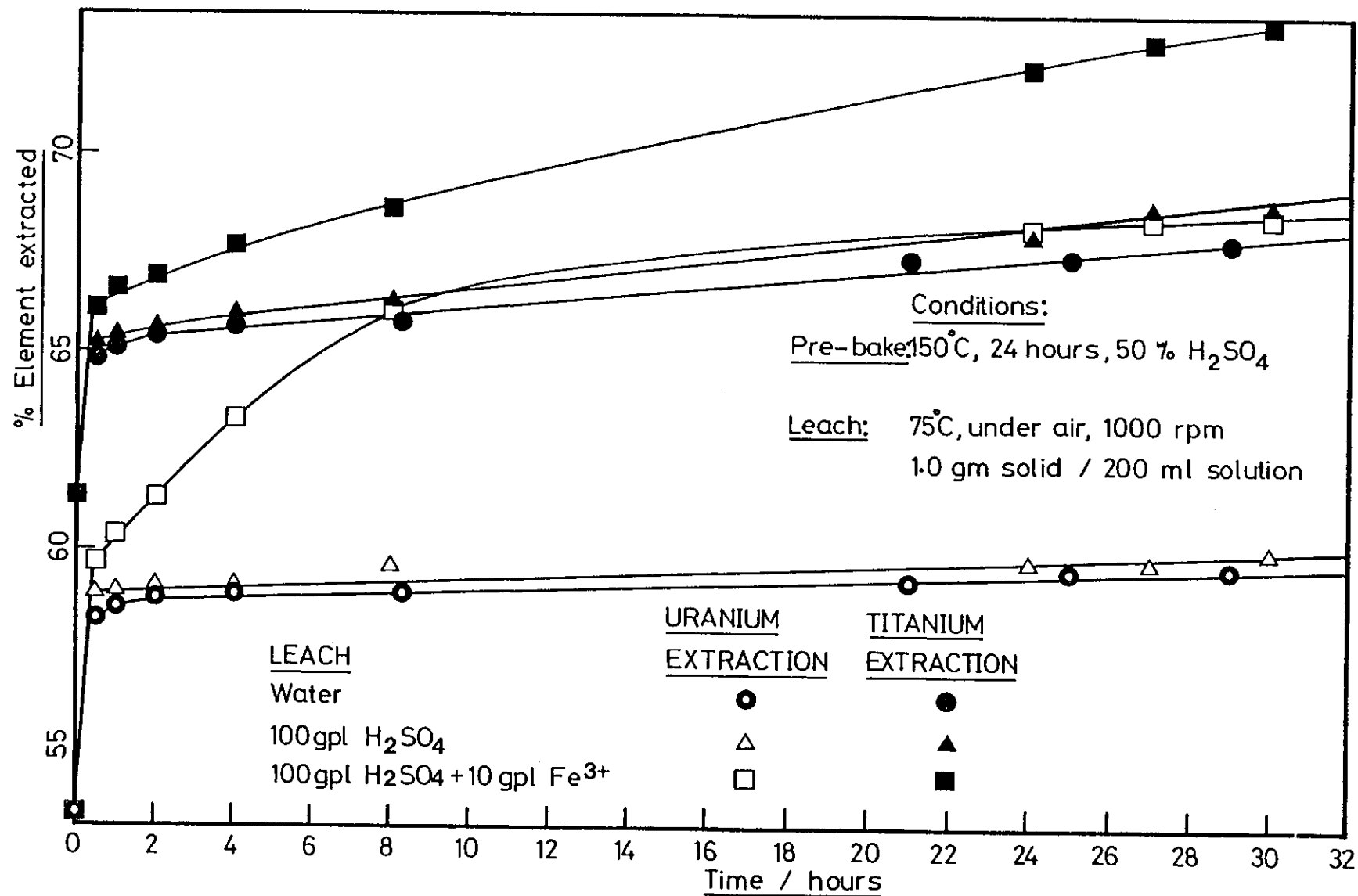
H_2O_2 and H_2SO_5 levels were monitored during the course of leaching runs by titration of sample aliquots (as described in "Experimental Procedures"). In both cases, it was found that decomposition was negligible during the course of runs, even up to 30 hours in length, and any disappearance of the oxidant could be explained in terms of the quantity of U(IV) oxidised to U(VI) and dissolved.

3.2.1.1.(x) Effect of pre-baking

A 3.0 gm sample of pure brannerite was subjected to an acid pugging process entailing baking a paste of the mineral with an equal weight of 50% H_2SO_4 for 24 hours, at 150°C . After baking, the paste was divided into three equal parts and three leach runs were undertaken using the following conditions:

- a) water leach
- b) 100 g/l H_2SO_4 leach
- c) 100 g/l H_2SO_4 + 10 g/l Fe^{3+} as oxidant

Results: Table 18, Graph 9.



Graph 9 Effect of acid-baking pure brannerite on leaching characteristics

The initial concentrations of uranium and titanium in the leach liquors indicated that brannerite had undergone considerable dissolution during the pugging process, with approximately 60% of the mineral having been dissolved in 24 hours. It is envisaged that an increase in acid quantity and/or time of pugging would have effected a virtually complete dissolution. It was clear that such conditions were the most encouraging encountered up to that point in experimental work, and they appeared to overcome the problem of the refractory nature of brannerite. However, in practice, the economics of such a process might render it quite impracticable due to the quantity of acid required to treat an ore. Further problems may also arise due to the simultaneous dissolution of other constituents of the ore.

Subsequent leaching of the brannerite pastes showed similar characteristics to the results of sections (i) and (ii) viz:

- there was very little dissolution in water (plus residual paste acid) alone, but an increase in acid concentration ($\equiv$ leaching in 100 g/l H_2SO_4) produced a marginal improvement.
- the presence of an oxidant during the leach process significantly improved the leachability.

The results indicate that pugging brought about a uniform dissolution of the mineral with the residue having been virtually unattacked. Any other type of attack (e.g. pitting) would have been expected to bring about a breakdown of the mineral structure, so enhancing subsequent leachability. This process did not appear to have happened.

Ti:U ratios indicate an approximately stoichiometric dissolution.

The data do not fit any of the leaching models.

3.2.1.2. Leaching_of_Doped_Brannerite

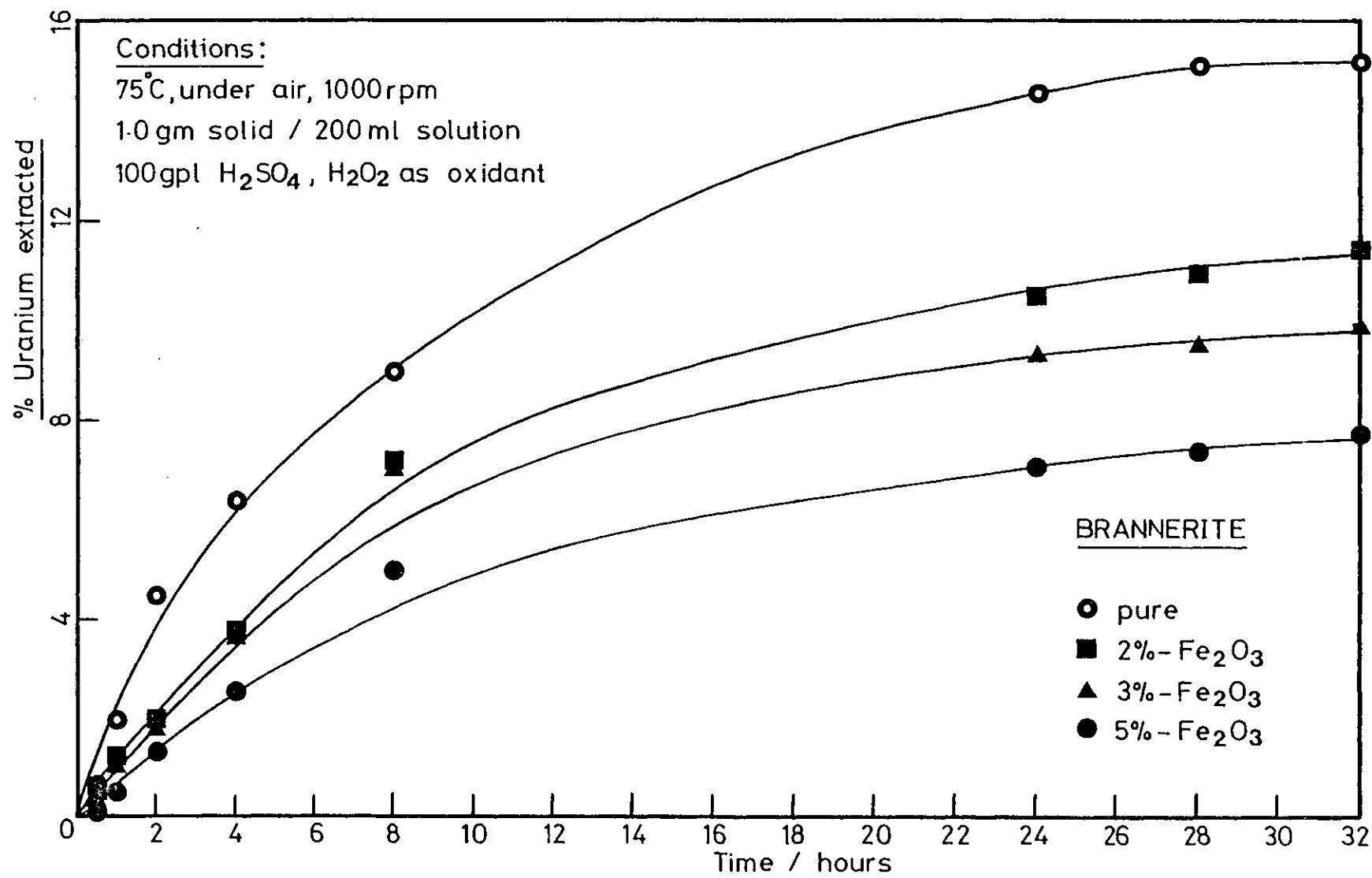
Brannerites containing 0, 2, 3 and 5 weight-percent Fe_2O_3 were prepared, as described in Sections 3.1.4. and 3.1.6. The effects of the doping additions on leachability were investigated under various conditions. It was found that, as with pure brannerite, acid oxidising conditions were required to bring about measurable dissolution. Hence, the preliminary experimental results, similar to those for pure brannerite, are omitted here.

In all cases, the powders were crushed and sieved. Artificial mixes were made up comprising (by weight): 25% of the -180+125, -125+90 and -90+63 micron fractions and 12½% of the -63+53 and -53+45 micron fractions. This process was adopted in an attempt to eliminate varying surface areas, from sample to sample, arising as a result of different sinter hardnesses. The samples were too small to permit any surface area measurements by gas adsorption.

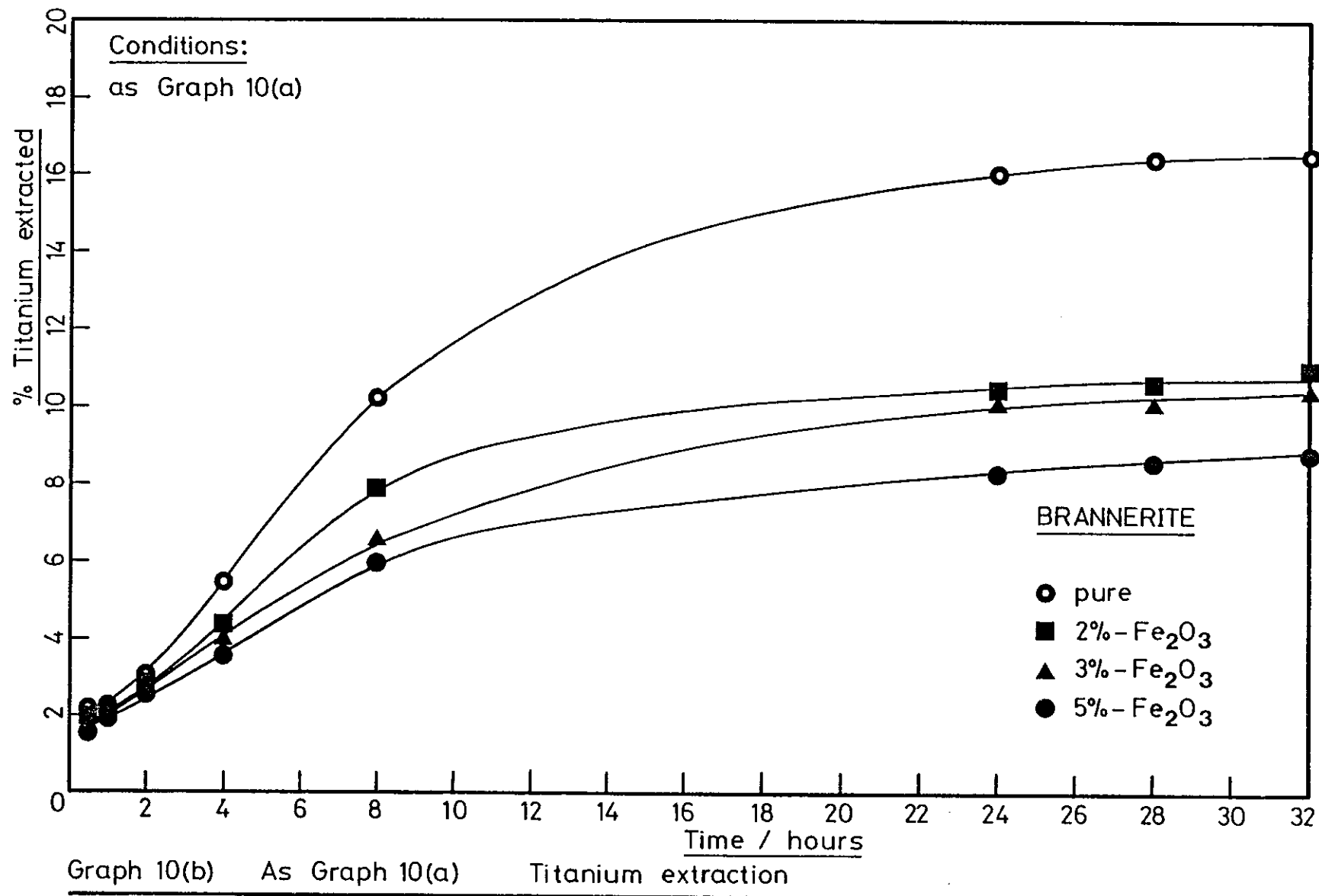
3.2.1.2.(i) Effect_of_stoichiometric_H₂O₂_oxidant_in 100_g/l_H₂SO₄

The effects of leaching the various samples in 100 g/l H_2SO_4 were investigated at 75°C, in the presence of H_2O_2 as an oxidant. The quantity of the oxidant added to each run was the calculated stoichiometric requirement for total U(IV) to U(VI) oxidation of the uranium contained within the mineral. Oxidant addition was made by eight equal aliquots at times $t = 0, \frac{1}{2}, 1, 2, 4, 8, 24$ and 28 hours of a 32 hour leach run.

Results: Table 19, Graphs 10(a),(b). Levels of dissolved iron, if any, were too low to be measured.



Graph 10(a) Effect of Fe_2O_3 -doping on leachability of brannerite in 100gpl H_2SO_4 , with stoichiometric H_2O_2 addition for U(IV) to U(VI) oxidation:- uranium extraction



Graph 10(a) shows typical leaching curves for uranium dissolution, with progressively decreasing rates with time. The curves indicate that the leaching rates and overall extractions from the minerals decreased as the Fe_2O_3 content increased.

Graph 10(b) shows a similar result for titanium extraction. One unusual feature noted was that the dissolution rates initially increased (up to time ~ 4 hours). After the initial period, the stoichiometric regime was established.

Ti:U ratios show that Ti was preferentially soluble in the early stages of leaching, after which, a regular dissolution behaviour was established. The strong complexing nature of Ti with H_2O_2 was believed to have provided an energetically favourable mechanism by which this process was achieved. Kinetic factors determined the stoichiometric dissolution; further Ti removal was hampered by the unleached U-rich layer and, therefore, could only proceed at the same rate as uranium extraction. This was a reverse, but similar mechanism, to that exhibited during ferric iron leaching of pure brannerite, discussed previously.

The behaviour observed, of increasing Fe_2O_3 content decreasing leachability, was first explained in terms of Fe dissolution resulting in the decomposition of the oxidant. However, H_2O_2 measurements by titration showed that decomposition of H_2O_2 was negligible and any disappearance was readily explained by the oxidation process required for the dissolved uranium. Thus, the chemical and/or structural nature of the doped mineral appeared to control its leachability and this will be discussed in the next section.

None of the leaching models were applicable.

3.2.1.2.(ii) Effect of sulphuric acid leaching with excess Fe^{3+}

Leaching tests were carried out on the doped brannerite at 75°C , using 100 g/l H_2SO_4 containing excess Fe^{3+} as the oxidant. The oxidant concentration was $\sim 8\times$ that required by stoichiometry. The method of addition and need for excess (to avoid availability problems) have been discussed previously.

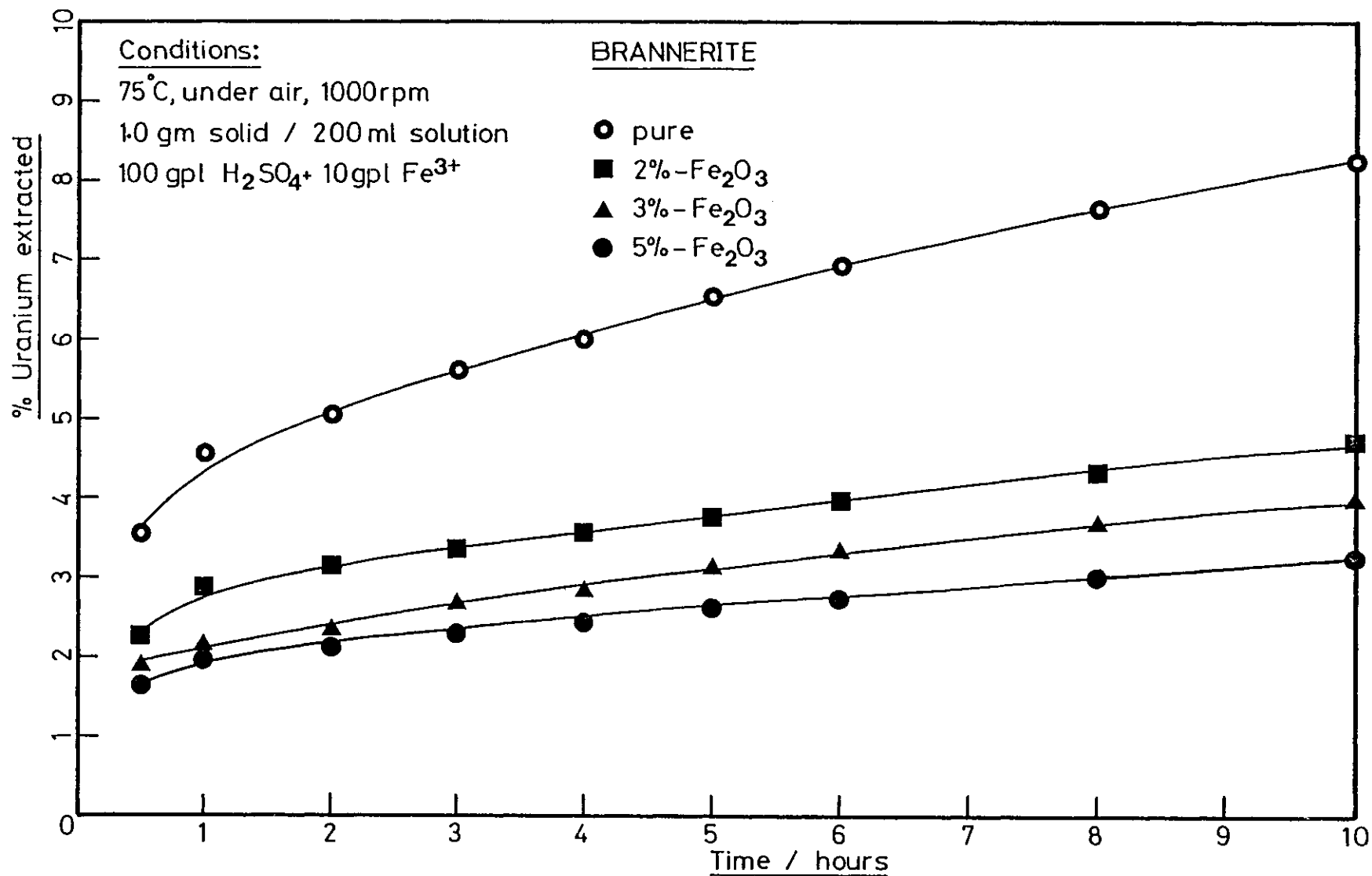
Results: Table 20, Graphs 11(a), (b), (c), (d). It was not possible to analyse for iron, for reasons outlined in the "Experimental Procedure".

The plots of dissolution of U and Ti, Graphs 11(a) and 11(b) respectively, show similar shapes of slowly decreasing rates of extraction with time.

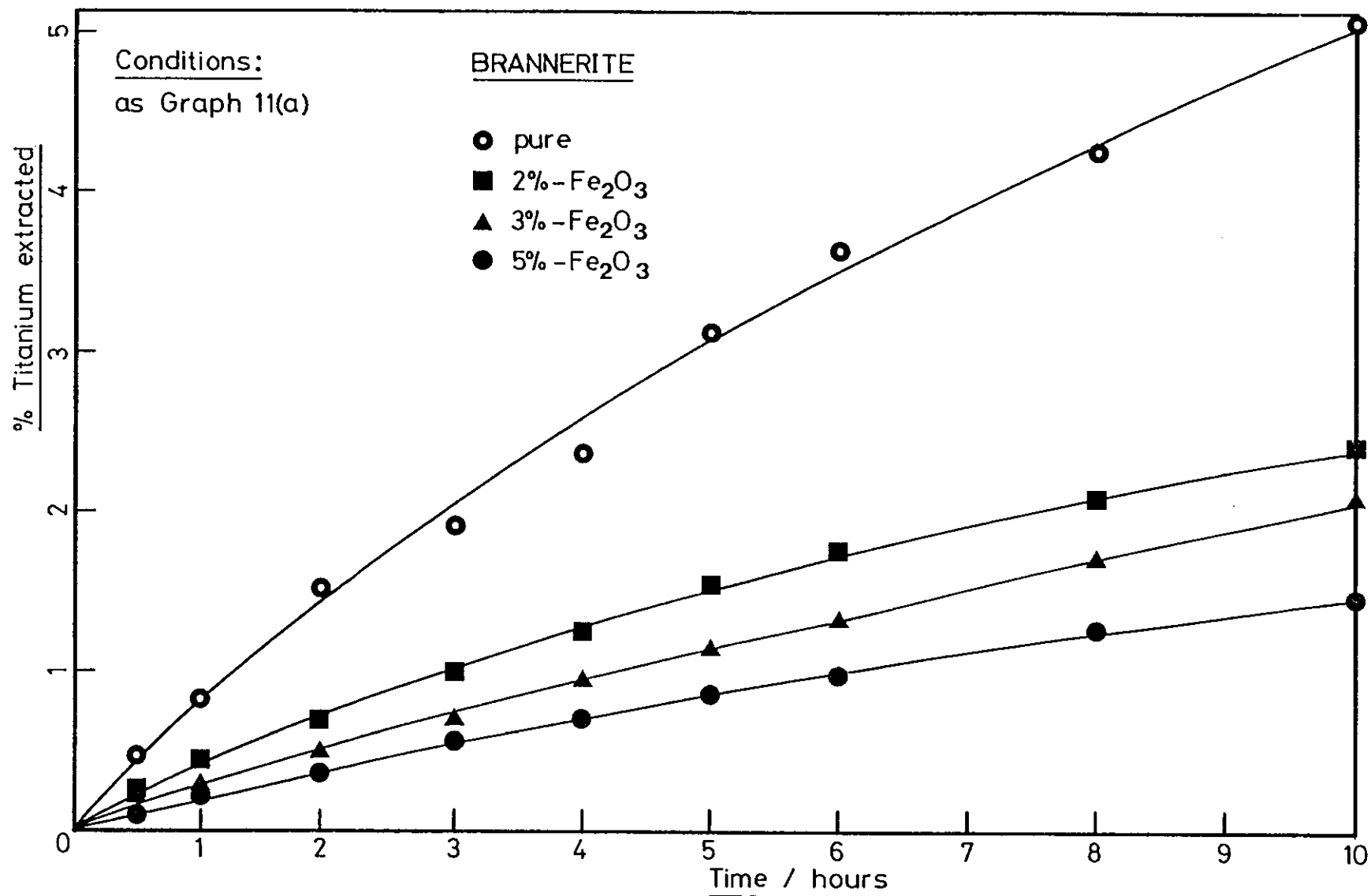
The plot of Ti:U ratio of extraction (Graph 11(c)) shows that U was preferentially soluble in the early stages of leaching, but the stoichiometric regime was approached. This was, presumably, due to kinetic factors similar to those experienced for pure brannerite leaching, and already discussed.

The only model that can be fitted to the data is the mixed kinetic model for uranium extraction. This was similarly found to fit data from leaching pure brannerite. A plot of $\Delta n \vee (t-t_0)/\Delta n$ is shown, in Graph 11(d), to demonstrate the excellent correlation of the data to the model, particularly after the initial stages of leaching. This would indicate that the dissolution mechanism of doped brannerite followed a similar path to that of pure brannerite.

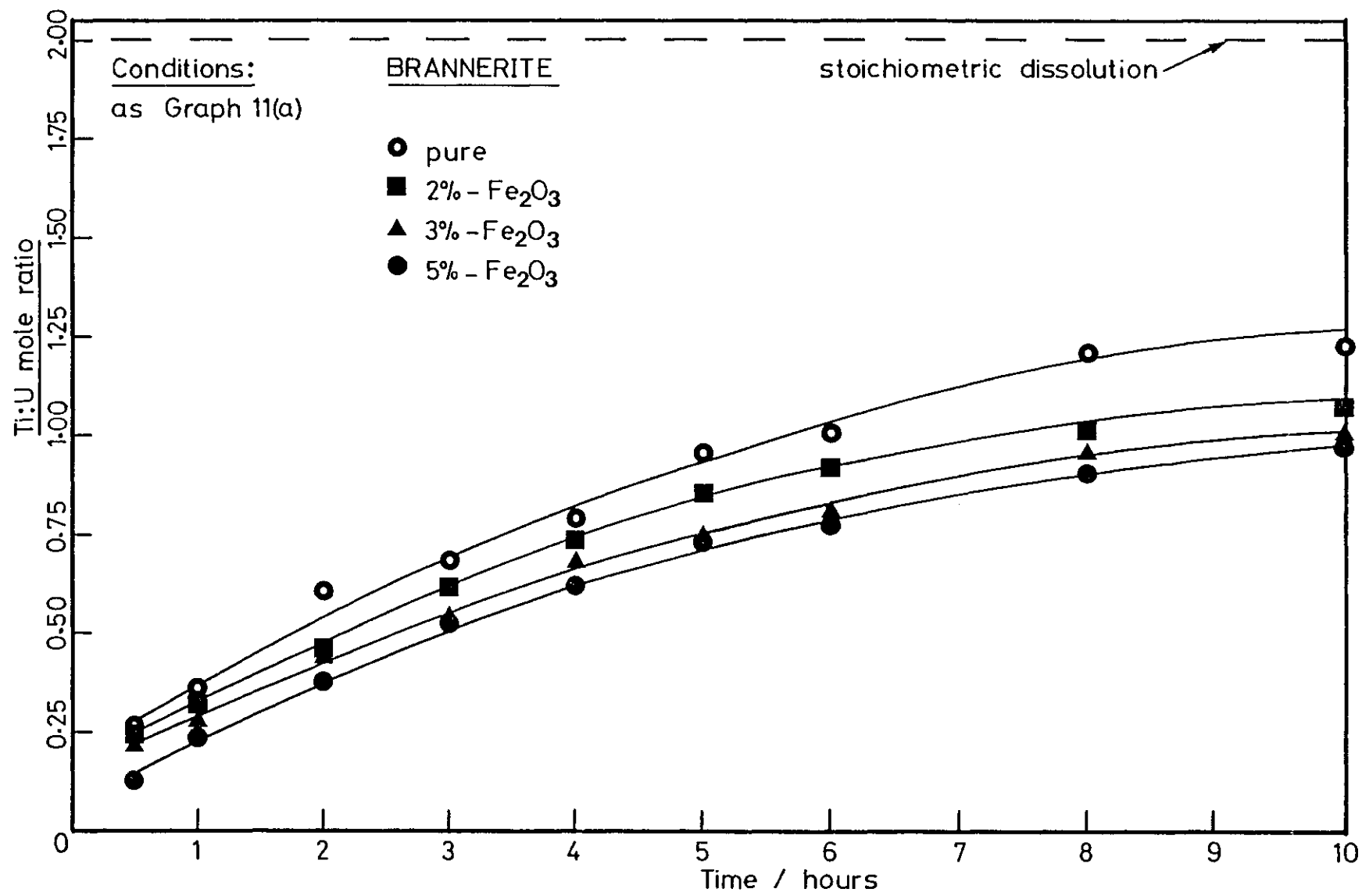
The dissolution curves, Graphs 11(a) and 11(b), show that leaching of the mineral was decreased by an increased presence of Fe_2O_3 , replacing UO_2 , in the



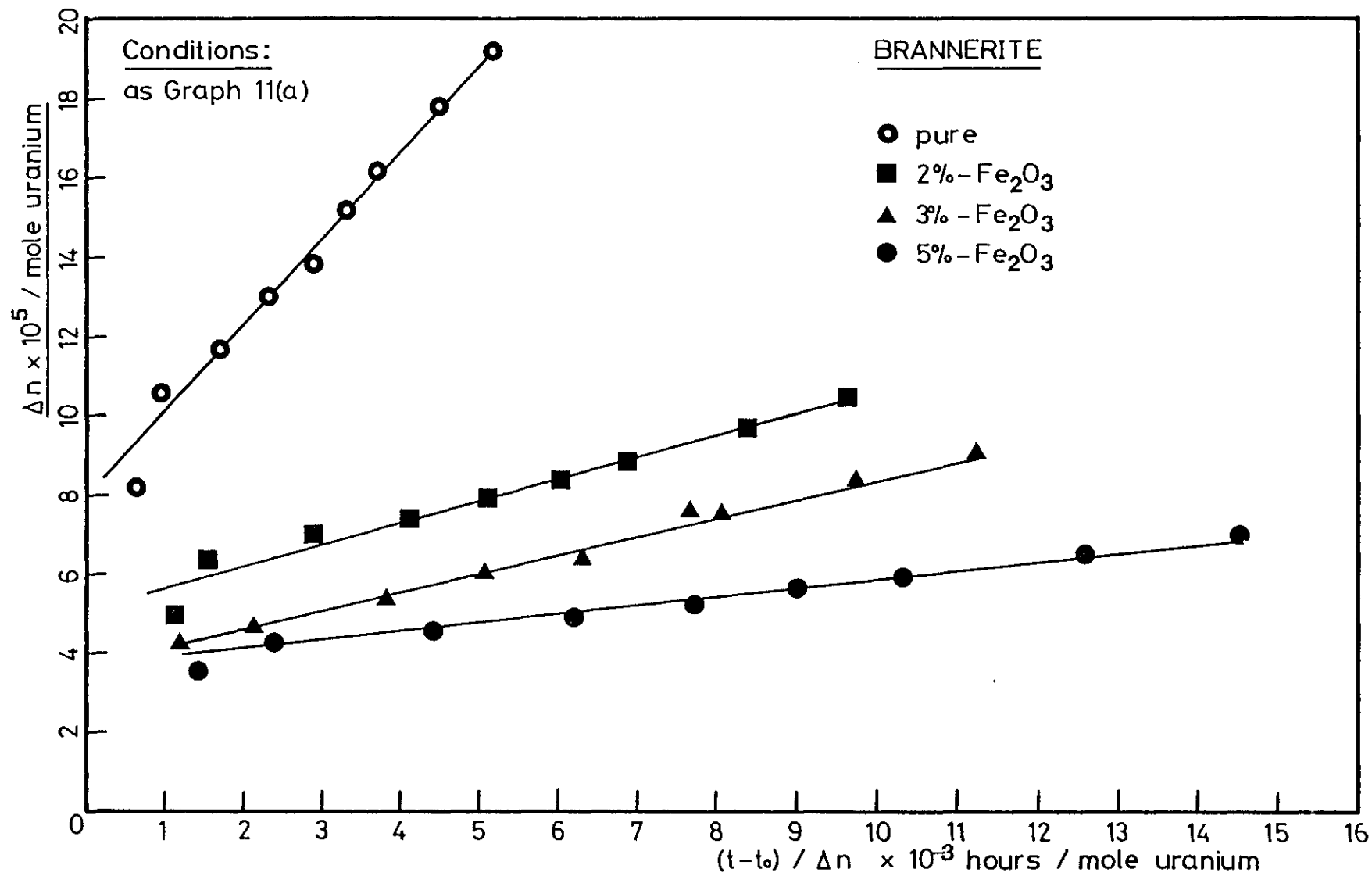
Graph 11(a) Effect of Fe_2O_3 -doping on leachability of brannerite in 100gpl H_2SO_4 + 10gpl Fe^{3+}
 (as excess oxidant) :- uranium extraction



Graph 11(b) As Graph 11(a) Titanium extraction



Graph 11(c) As Graph 11(a) Ti:U mole ratio of extraction



Graph 11(d) As Graph 11(a) Plot to confirm applicability of mixed kinetic control model,
 Δn v. $(t-t_0) / \Delta n$

brannerite lattice. This behaviour can be explained by a combination of chemical and structural effects. It has already been shown that the introduction of Fe_2O_3 increased the hardness of the sinter (determined by increased difficulty in crushing and grinding). This suggests that the bonding within the doped mineral was enhanced by the presence of Fe_2O_3 .

The introduction of the relatively small ferric ion into doped brannerite has been shown to produce a slight shrinking of the lattice. The associated vacancies and interstitial ions produced close-packing and, hence, a barrier to easy ion movement, usually required for leaching procedures.

Microstructural changes on doping with Fe_2O_3 indicated an enhancement of consolidation of the sinter, producing regular grains with less porosity. This helped to eliminate the network nature of pure brannerite, with the associated "bridging-sites", and the resultant enhanced leaching rates, as determined previously. The overall effect was that the crushed doped brannerite powders had become progressively more solid (less internal porosity) and, hence, less leachable as the Fe_2O_3 content was increased.

3.2.1.3. General Discussion - Leaching Synthetic Brannerite

X-ray diffraction studies of leach residues showed that the structure of the brannerite did not change on leaching. The observation confirmed the chemical analyses which showed dissolution to occur, in general, by a stoichiometric mechanism. Leach residues extracted during the very early stages of a run (or from non-stoichiometric leaching runs), when U or Ti dissolution predominated, showed no change. This was an indication that any variation in solid composition was on a microscopic scale, which was

not detected by the technique.

The activation energies obtained for U and Ti extractions give an explanation as to why two of the leaching models showed no correlation with the data. Both models assume a diffusion-controlled process. However, it can be concluded from E_a values that leaching proceeded by a mixed chemical/diffusional controlled mechanism, or a totally chemical controlled process, dependent on temperature. Clearly, other factors were also involved in invalidating the models. Such factors included mixed particle sizes and irregular geometrical shapes; a contrast to the ideal, equisized spheres assumed during model derivation.

The activation energy values found for uranium extraction at high temperatures suggest that dissolution was by a mixed control mechanism. This has been borne out by considerable correlation with the model for mixed control outlined in the literature survey. Variations could be explained by the non-ideal conditions of sample geometry, different particle sizes, etc.

The variation in E_a (U) with temperature from 137 kJmole^{-1} to 36 kJmole^{-1} , on a temperature rise from 30°C to 90°C , can be explained by a change in leaching mechanism. A mixed chemical/diffusion control operated at high temperatures. The role of the diffusional factor decreased with temperature until total chemical control took over.

The activation energy for titanium dissolution, however, varying from 40 kJmole^{-1} at 30°C to 100 kJmole^{-1} at 90°C , is a surprising result. A mode of dissolution is proposed, in which, an increasing kinetic barrier to Ti ion removal was present, on the temperature being raised. As the Ti:U ratios suggest, the early stages of leaching showed uranium to be the preferentially soluble

ion. It is envisaged that uranium dissolution left behind a Ti-rich surface layer, in which, the Ti was closely bound by the residual oxide sublattice. The production of the residual distorted layer hindered subsequent uranium extraction. The rate decreased until it was controlled by the rate of titanium extraction, resulting in a stoichiometric dissolution regime. Increased temperature increased the rate of production of the residual layer. This, in turn, increased the rate of hindrance to Ti dissolution, the kinetic barrier, which was reflected by the rise in E_a .

The process of leaching is dependent on the breaking of bonds within the mineral lattice, to liberate metal ions. In a refractory mineral, such as brannerite, the metal-oxygen bonds have high energies. The bond energies associated with the U-O and Ti-O bonds in brannerite have not, to the author's knowledge, been determined. In acid media, it was generally found that uranium was preferentially soluble (until a kinetic mechanism took control), so, it can reasonably be concluded that the Ti-O bond was stronger than the U-O bond in the synthetic brannerite.

There was an exception to this rule. In the presence of H_2O_2 , the roles of U and Ti dissolution were apparently reversed and Ti was preferentially soluble. This change in behaviour is believed to have been brought about by the strong complexing nature of H_2O_2 with Ti, providing an energetically favourable route for preferential Ti extraction. It is suspected that the E_a variation experienced with acid/ferric iron solutions would be reversed with acid/ H_2O_2 media, although this hypothesis was not investigated further.

During the course of the tests on "effect of particle size", it was found that the large, porous particles became fragmented on leaching. The attack

had been preferential at the "bridging-sites" between fairly solid areas. Such a preferential attack is consistent with the mechanism of pitting, which is characteristic of electrochemical dissolution processes. Nicol et al.⁽²⁶⁾ have shown that dissolution of UO_2 , in oxidant-containing acid media, occurs by an electrochemical mechanism in which anodic oxidation of UO_2 is coupled to cathodic reduction of the oxidant at the oxide surface. It is generally accepted that the oxidation of U(IV) to U(VI) takes place prior to the dissolution step. The relative order of efficiency of various oxidants was explained on an electrochemical basis. Although an investigation into the possibility of an electrochemical attack was not pursued, the activation energies for the dissolution processes do not rule out such a mechanism. This should be borne in mind if future work is carried out on brannerite.

Tied in with the electrochemical nature of dissolution processes is the electronic nature of the solid. Many minerals exhibit semi-conductor properties due to the presence of impurity ions, particularly where there is a valency difference between the parent and the doping ions. Clearly, brannerite doped with trivalent iron ions, replacing four-valent uranium ions, might come into this category. This seems to be confirmed by very recent "Science Citation Index" references to Russian work in this field, using rare doping elements. Further information on the subject is not yet available. Regrettably, in the current work, the porous nature of the synthetic brannerite sinter prevented any determination of its semi-conductor properties.

In practical uranium leaching operations, acid levels have to be maintained at certain values to prevent precipitation of metal values. During the present work, the acid levels were high and the metal ion concentrations in solution low, thereby eliminating any solubility

problems. For example, solubility tables produced by Monhemius⁽⁵⁷⁾ show that titanium hydroxide will not precipitate at pH 1 until the log (metal ion activity) exceeds -1. The current leaching studies did not produce metal levels in solution even approaching this value, and the pH ranges used were lower than pH 1.

3.2.2. LEACHING OF A NATURAL BRANNERITE ORE

A short series of experiments was carried out on the natural brannerite ore supplied from Rio Algom Mines. Sample preparation was as described under "Experimental Procedure". The standard leaching conditions can be summarised:

- H_2SO_4 ; of stated molarity,
- temperature; 25°C or 75°C ,
- 20 gm solid; -100 mesh,
- 200 ml solution,
- } 10% slurry,
- sample by 10 ml aliquot (unless stated),
- under air (unless stated); atmospheric pressure,
- agitation, at 1000 rpm, uplift stirrer,
- oxidant; added as stated.

Exact leaching conditions are given in Tables and Graphs of results. The uranium extractions are presented in two ways: either as a percentage of the total uranium presence, assuming an assay of 0.0855% U, or as mg U extracted per 20 gramme ore sample.

3.2.2.1. Vigorous attack

The aim of the experiments was to severely attack the ore at 75°C , for ~6 hours, under three leaching regimes, to determine the extent of uranium extraction. The three media were:

- a) 10% Caro's Acid (low peroxide)
- b) 100 g/l H_2SO_4
- c) pre-bake with w/w concentrated H_2SO_4 , at 150°C , for 10 hours, followed by leaching with 100 g/l H_2SO_4 .

Results: Table 21, Graph 12.

The results show that, after 6 hours leaching, the same total uranium extractions had been achieved. Correlation of these results with the results of XRF analyses, on the residues, indicated that the total uranium content of the ore was 0.0855% U. It appeared that well over 90% of the uranium content of the ore could be removed by severe attack.

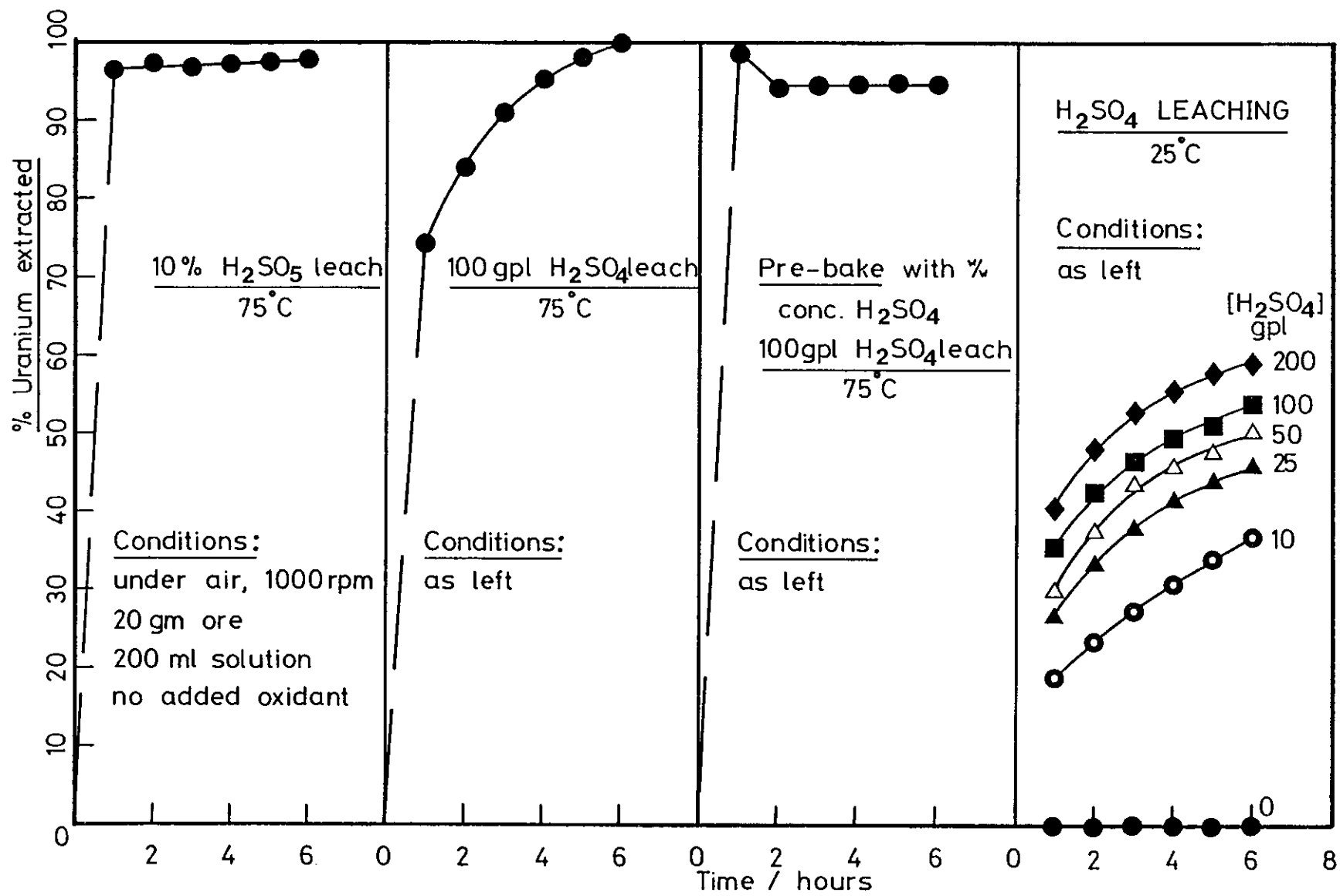
Two other results were noted:

- addition of the ore to the liquor produced a temperature rise of between 5°C and 10°C, indicating that a constituent of the ore had exothermic dissolution characteristics.
- at the start of each run a strong smell of H₂S was noticed, which persisted for 2 to 3 minutes. This observation signified that reducing conditions prevailed in the leach liquor during the early stages of leaching. This was a particularly important result since, in an oxidative leach, an oxidant added at the start would have been needlessly used up. Oxidant should only be added when oxidising conditions develop. Such behaviour is typical of ores which contain pyrite-pyrrhotite. The phenomenon warranted further investigation, which is discussed below.

3.2.2.2. Leach liquor characteristics

The leach liquor characteristics can be summarised as:

- a) acid consumption; the quantity of acid, destined for leaching, which is wasted due to neutralisation by bases in the ore.



Graph 12 Effect of leaching Rio Algom brannerite ore under various conditions

b) the acid concentration which must be maintained to prevent reprecipitation of dissolved metal values.

c) the point at which oxidising conditions develop in a leach.

The acid consumption of the ore was found to be equivalent to 25 gm, 93% H_2SO_4 per kg of ore (or 25 kg, 93% H_2SO_4 per tonne of ore). The method used was to "leach" 75 gm of ore in 100 g/l H_2SO_4 , at low temperature (25°C). The conditions were chosen to ensure low uranium extraction, so that any acid consumed was as a result of neutralisation and dissolution of non-values. As total titration to find the acid concentration after leaching would have caused reprecipitation of metal salts, stock acid and final liquor were titrated against NaOH to pH 1.8, exactly, and the difference in acid concentration regarded as a measure of the total acid consumption. This method gives only a rough guide to the actual value, and consumption would be expected to rise with leaching temperature.

The second result was evaluated using a vigorous leach of 100 g/l H_2SO_4 , at 75°C , on a 75 gm sample, in 200 ml of solution (i.e. 37.5% slurry). The resulting leach liquor was titrated against standard NaOH solution up to the first sign of precipitation. Having taken into account the acid consumption of the ore, it was found necessary to have a final concentration of acid of >18 g/l H_2SO_4 for a 37.5% slurry. It must be stressed that this is a minimum level and actual operations use upwards of 50 g/l. The value is exceedingly dependent on slurry density and temperature.

The point at which oxidising conditions prevailed was found by monitoring the E_H of a leach run (75°C , 100 g/l H_2SO_4 , 10% slurry), by means of an immersed electrode. Although it was reported⁽²⁴⁾ that reducing

conditions prevail during the first few hours of commercial leaching, the experiment showed that oxidising conditions were obtained after 2-3 minutes of the leaching run. This would indicate that oxygen transfer within the leaching vessel used was considerably greater than that in a pachuca. In subsequent leaching runs, it was decided to "play safe" and oxidant additions were made after 5 minutes of leaching, although they were still recorded as "at the start".

3.2.2.3. Effect of sulphuric acid concentration on leaching

The effects of leaching the natural ore in 0, 10, 25, 50, 100 and 200 g/l H_2SO_4 were studied at 25°C , in the absence of added oxidant.

Results: Table 21, Graph 12.

As expected, increases in acid concentration produced increased initial uranium leaching rates and overall uranium extractions. The leaching curves have similar shapes of continuously decreasing rates with time. Distilled water failed to dissolve any significant quantity of uranium, indicating that there was no uranium mineral in the ore that was soluble.

3.2.2.4. Effect of various oxidants on leaching

An investigation into the leaching characteristics of the ore in 50 g/l H_2SO_4 , at 75°C , in the presence of various oxidants, was undertaken to monitor their effects on leaching rates and overall extractions of uranium. The following oxidants were chosen for study:

- a) normal atmosphere, control leach.
- b) Caro's Acid, one addition at the start of a run.

- c) Caro's Acid, stepwise addition throughout a run.
- d) H_2O_2 , one addition at the start of a run.
- e) H_2O_2 , stepwise addition throughout a run.
- f) KClO_3 , predissolved in acid, at start of a run.
- g) MnO_2 , at start of a run.
- h) oxygen, leach carried out under O_2 atmosphere.

However, it must be stressed that the principal oxidant of U(IV), during leaching, is the Fe^{3+} ion. From previous leaches, it was estimated that the final leach liquors contained typically ~ 10 g/l iron. Thus, the oxidants could have acted directly on U(IV) or indirectly, via the ferric-ferrous couple followed by oxidation of U(IV), or by a combination of the two. ClO_3^- and MnO_2 act as oxidants for $\text{Fe(II)} \rightarrow \text{Fe(III)}$ only; they do not oxidise U(IV) directly.

Rio Algom normally use the air jet of a pachuca as the source of oxidant, so no guide as to the oxidant requirement was available. However, Denison Mines leach a brannerite ore using 1-2 lb of NaClO_3 per ton ore as the oxidant. This was used as the guide and all experiments were carried out (with the exception of the oxygen-atmosphere leach) so that the [O] content of the oxidant, added during the course of a leach, was equivalent to adding 2 lb of NaClO_3 to 1 ton of ore. 2 lb NaClO_3 per ton ore is equivalent to 5.043×10^{-3} M [O] per 20 gm ore sample, where [O] is the oxygen available for oxidation purposes.

In all cases (except the oxygen leach), the total amount of [O] added as the oxidant was the same, whether added all at the beginning of a run or in stages. When the [O] was added stepwise, it was added after sampling, in six equal aliquots, at the times indicated on the table of results. In the case of leaching under oxygen,

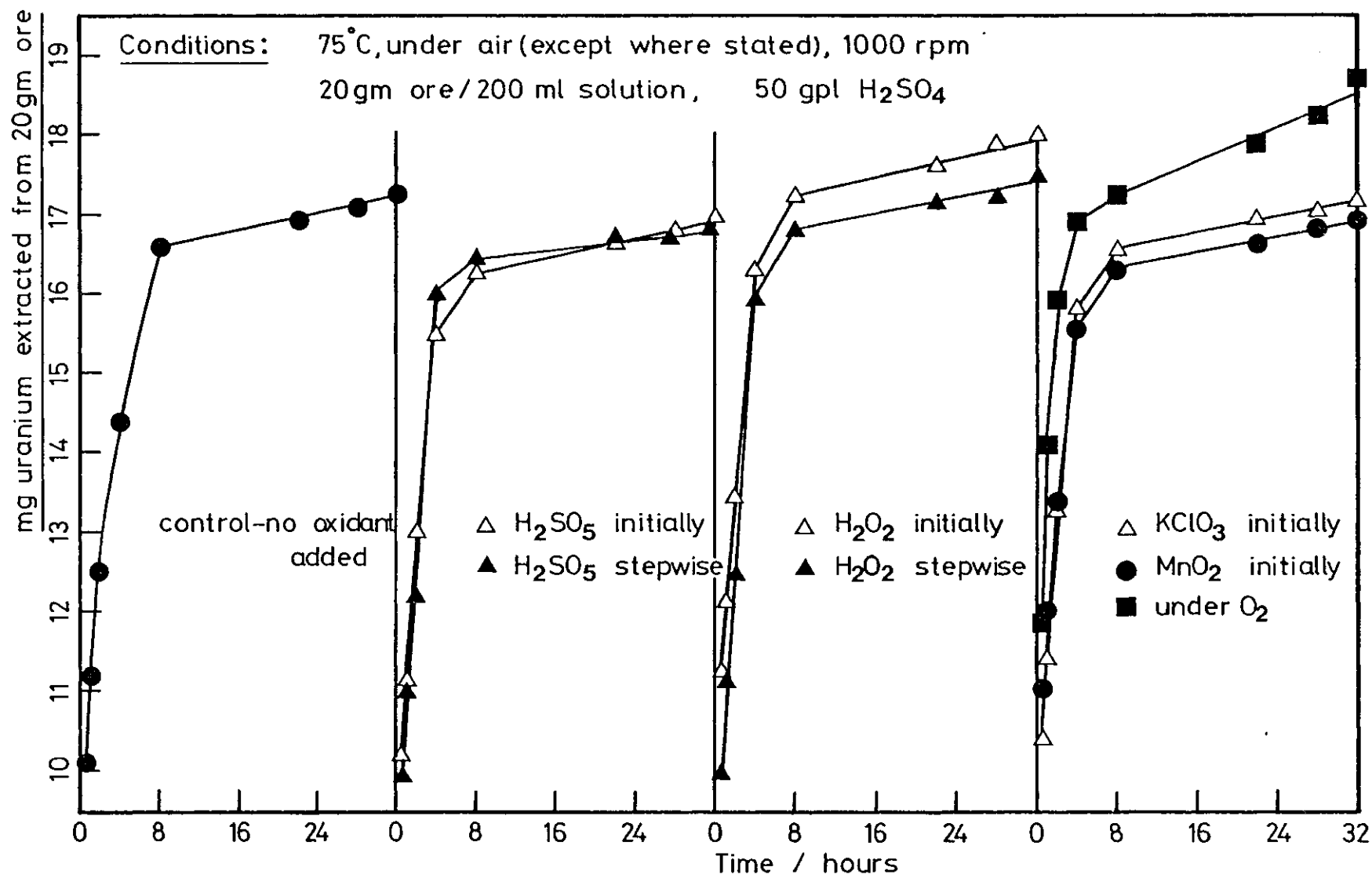
there was effectively an infinite [O] available for dissolution and, hence, oxidation in the liquor.

Results: Table 22, Graph 13.

The curves all show similar characteristics of two distinct stages of leaching. The first stage, during which most of the uranium was extracted, was rapid and approximately linear. The second stage was much slower, indicating difficulty in removing the last traces of uranium. The transition between fast and slow stages occurred between 4 and 8 hours, in all cases. In all the leaches, the addition of an oxidant increased the initial (fast stage) leaching rate but the second (slow) stage of leaching proceeded at approximately the same rate (except in the case of the oxygen leach).

The effects of individual oxidants, in comparison to the control leach in the absence of any additional oxidant, can be summarised:

- with Caro's Acid; the initial rate was increased, independent of single or stepwise addition. The transition to second stage leaching occurred earlier than in the control, but the rate was unchanged. Less uranium (although not significantly) appeared to be extracted than in the control. There was no real difference in adding Caro's Acid as a batch, at the start of a run, or in stages.
- with hydrogen peroxide; the initial rate was increased, with single-batch addition producing a marginally faster first stage rate than stepwise addition. The transitions to the second stage took place earlier than in the control, but the second stage rates remained unchanged. More uranium was extracted than in the control; stagewise addition produced a marginally better



Graph 13 Effect of various oxidants on the leaching of natural brannerite ore
(Rio Algom) at 75°C, with 50 gpl H₂SO₄

yield of uranium, whilst single-batch addition a noticeably higher yield of uranium.

- with KClO_3 (which was expected to be equivalent to NaClO_3 , as used by Denison Mines); the initial leaching rate improved, the transition occurred earlier, the second stage rate remained unchanged and the total extraction of uranium was unchanged.
- with MnO_2 ; the initial leaching rate improved, the transition occurred earlier, the second stage rate remained unchanged but the total uranium extracted was marginally reduced.
- under an oxygen atmosphere; the first stage leaching rate was vastly improved. The transition to the second stage occurred much earlier and after a considerable increase in uranium extraction. The second stage rate was much faster than the control. The overall uranium extraction showed a marked improvement.

The results indicate that the most effective oxidant was oxygen gas above the leach solution, so confirming Rio Algom's mode of oxidation. Hydrogen peroxide added in an initial single batch was the next best. There was very little to choose between H_2O_2 (stepwise addition), Caro's Acid, MnO_2 or KClO_3 . (This would be the trend if the actual oxidant was Fe(III) , in all cases).

The actual choice of oxidant in a practical leach will probably be governed by several factors; for example, ore mineralogy, oxygen is readily available in an air-agitated pachuca, H_2O_2 is easily decomposed in the presence of some transition metals and so may only serve as a means of putting oxygen into solution via a costly material, Caro's Acid would be more stable than H_2O_2 under such circumstances, etc.

3.2.2.5. General discussion

It has been previously outlined, in the literature survey, that leaching of a natural brannerite mineral is principally dependent on the mineralogy of the deposit. Rio Algom ore from Elliot Lake contains brannerite as the predominant uranium mineral with smaller quantities of monazite, uraninite and other uranium-bearing minerals. Monazite is more refractory than brannerite whilst uraninite is fairly easily dissolved. There is also some evidence of alteration of the brannerite mineral on exposure to weathering, which makes the ore easier to leach⁽²⁴⁾. Thus, it was not possible to isolate brannerite as a unique material on which to do leaching tests. The results obtained reflect the nature of the ore as a whole.

The above observations lead to the conclusion that correlation between leaching natural brannerite and a fundamental study is limited, and results must be treated with care. However, it is clear that high temperatures, high acid concentrations and the presence of an oxidant are essential requirements in the leaching of any form of brannerite.

SECTION 4

SUMMARY OF RESULTS AND CONCLUSIONS

It was the aim of this project to undertake a fundamental leaching study of the complex uranium titanate, brannerite, in the hope that some of the difficulties encountered in commercial operation of extraction of uranium, from brannerite-containing ores, might be explained. Like all uranium minerals, brannerite abundance, even in a rich deposit, is relatively small.

Typical uranium contents are of the order of 0.1% (although, some ores now known run at about 2-5% U), which will include the associated uranium-bearing minerals. Thus, it is physically impossible to isolate brannerite, as a unique material, on which to do such a study. Several other factors compound the problem; brannerite can show a wide variation in chemical composition and varied degrees of alteration, or metamictisation. Thus, it was necessary to synthesise a pure mineral, which was iso-structural with natural brannerite, from which the basic leaching characteristics could be determined.

Of the various literature reports on brannerite synthesis, only one method was repeated with success. The route was a pyrosynthesis, to a sinter, involving a solid-state, diffusional mechanism. However, pure brannerite product was only achieved under considerably more rigorous conditions than those reported. The successful pyrosynthesis required conditions of 1400°C , under an oxygen-free argon atmosphere and a time of synthesis of six weeks. The reactant material consisted of a consolidated mix of $(\text{UO}_2 + \text{TiO}_2)$, in the mole ratio 1:2, contained in an inert, re-crystallised alumina boat. The product was ~100% pure brannerite sinter, which was confirmed to be iso-structural with natural brannerite.

The mechanism of sintering was confirmed to be two-stage; the first stage was an interchange of U and Ti ions between the oxides, whilst retaining the original UO_2 and TiO_2 crystal lattices (no trace of a product could be found). The first stage of sintering indicated that a chemical reaction, to a ternary oxide, was not required; it was purely a diffusional interaction. The second stage, the reaction to the ternary oxide UTi_2O_6 , was achieved by re-ordering of the sinter lattices.

Reported methods of manufacture of brannerite by melting the constituent oxides could not be reproduced. Contamination from the furnace proved to be a major problem. Melting of the sintered brannerite, an attempt to form a fully dense mineral, proved unsuccessful. Reformation of the U and Ti dioxides and the introduction of contaminants occurred. The result indicated that the free energy of formation of brannerite was positive at the estimated temperature of melting, 2300°C . The introduction of contaminants appeared to hinder brannerite reformation on subsequent annealing.

Chloride-melt techniques were not tested due to the high probability of impurity entrainment. The lack of success with melting techniques meant that leaching studies could only be carried out on the brannerite sinter.

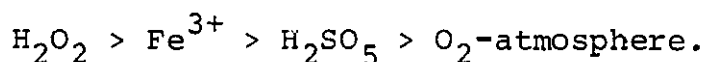
Iron was successfully incorporated into a brannerite sinter, as a controlled impurity, in an effort to reproduce some of the natural variations in brannerite, away from the idealised chemical composition.

The physical nature of pure brannerite sinter was investigated and shown to be exceedingly porous. The sinter had a network (pumice-stone) appearance on a microscopic scale. The introduction of iron into the sinter produced a dramatic change in the microstructural nature of the product. Fe_2O_3 had markedly enhanced the

sinter reaction, producing a decrease in porosity and an overall consolidation of the brannerite. On a crystallographic scale, the presence of iron had resulted in a shrinkage of the crystal lattice. The effect was explained in terms of the small ionic radius of the ferric ion (in comparison to the uranium ion), the lower valency state and the excess number of Fe ions, producing vacancies in the oxide lattice. All these factors combined to condense the lattice. It was found that the hardness, a measure of bond strength, increased with increasing iron addition.

The results of the leaching studies on brannerite can be summarised as follows (pure synthetic brannerite, unless stated).

1. Acid leaching; even high temperature and high acid concentration produced negligible brannerite dissolution, in the absence of an oxidant.
2. The presence of an oxidant was essential to achieve any significant amount of mineral dissolution. Uranium extraction was dependent on the U(IV) in the mineral being oxidised to U(VI), prior to removal. The Ti(IV) in the mineral dissolved in the tetravalent state. Increased levels of oxidant, up to ~8-10 times the stoichiometric requirement for U(IV) to U(VI) oxidation, increased leachability. Above these levels, oxidant availability was not rate-controlling.
3. Increasing acid concentration, for a constant oxidant level, brought about an increase in leaching rate and overall metal extraction.
4. The order of effectiveness of the oxidants investigated was:



The excellent performance shown by H_2O_2 was best explained in terms of the strong complexing nature of H_2O_2 with titanium.

5. Measured Ti:U ratios (of metal in solution) indicated that, in the early stages of leaching, uranium was preferentially soluble. However, the stoichiometric value of 2.0 was approached as leaching progressed. It was proposed that, in the early stages of leaching, uranium was more soluble than titanium so a microscopic, Ti-rich residue was left on the surface. This provided a kinetic barrier to further U dissolution and, hence, a balance was achieved between the two dissolution processes - the stoichiometric regime.

6. An investigation of the effect of temperature, on acid/ferric ion leaching, showed that increases in temperature resulted in accelerated leaching rates and greater overall mineral dissolutions.

Measurement of activation energy, at 5% uranium extraction, showed E_a to vary with temperature from 137 kJmole^{-1} at 30°C to 36 kJmole^{-1} at 90°C . These results indicate that the mechanism of dissolution of uranium was temperature dependent. The mechanism varied from being under total chemical control at low temperatures to being under mixed chemical and diffusional control at high temperatures. The importance of the diffusional control component increased with temperature. Activation energy values for titanium dissolution showed the reverse trend, with $E_a \sim 40 \text{ kJmole}^{-1}$ at 30°C and $\sim 100 \text{ kJmole}^{-1}$ at 90°C . This phenomenon was concluded to have occurred due to increased difficulty of Ti dissolution; a result of a kinetic barrier having been set up by enhanced U dissolution rates, on increasing temperature. The kinetic barrier was believed to have been due to alteration of the lattice on U removal, so inhibiting Ti extraction.

Increased temperature led to increased rates of alteration of the lattice (equivalent to the kinetic barrier to Ti dissolution) and, hence, to an increase in E_a . However, E_a for U dissolution must equal E_a for Ti dissolution in the stoichiometric regime.

7. The use of hydrogen peroxide as an oxidant reversed the above trends and comparable, but reversed mechanisms, can be postulated because of the formation of thermodynamically stable complexes between Ti^{4+} and H_2O_2 .

8. It was observed that larger particles produced better initial leaching rates (and overall metal extractions), but the subsequent leaching rates were virtually independent of particle size. The results were explained in terms of preferential and rapid leaching of "bridging-sites" connecting the sinter network, producing fragmentation. The biggest particles, having a higher concentration of "bridging-sites", showed the best leachability. Fragmentation standardised the particle sizes, leading to approximately equal secondary leaching rates. Microscopic examination of the particles supported the theory.

9. Acid-baking processes were shown to be the only method of achieving substantial brannerite dissolution (~60%), in a reasonable time. Subsequent leaching of the pastes produced only marginal improvement in extraction. This indicated that the pugging dissolution was uniform and there was no overall destruction of the crystal structure.

10. Comparison of H_2SO_4 , HCl and HNO_3 gave roughly similar leaching abilities, with HNO_3 being marginally the best.

11. Such high acid concentrations and oxidation potentials were required, to effect leaching, that no discernable changes could be monitored during the course of the runs.

12. Fitting of simple leaching models generally proved unsuccessful due to the invalid assumptions, of the derivations, for the conditions encountered. However, a mixed diffusion/chemical control model fitted the uranium extraction data for high temperature acid/ferric iron leaching, so confirming the modes of control predicted from E_a values.

13. Doping of brannerite with Fe_2O_3 decreased leachability in the media employed. The behaviour was attributed to the change in structure on doping (consolidation of the sinter and a more closely-packed crystal structure) and to an increase in bond strength (indicated by the increased hardness on crushing).

14. All the leaching runs, using synthetic brannerite, showed similar extraction curves. They all exhibited progressively decreasing rates with time.

15. Leaching of a natural brannerite ore showed that vigorous attack, or high temperature acid leaching with an oxidant present, resulted in nearly all of the uranium being extracted. Various oxidants had no significant order of effectiveness, with one exception. An oxygen-atmosphere leach produced by far the fastest rate and highest overall uranium extraction. It was believed that oxidation of U(IV) to U(VI) occurred via the ferric-ferrous couple and other oxidants, therefore, acted indirectly.

16. The difficulty in isolating natural brannerite as a unique mineral makes comparison of data from the fundamental study, with actual ore data, somewhat doubtful. What is clear, however, is that high temperatures, high

acid concentrations and high oxidation potentials are required to effect sensible leaching of the refractory brannerite mineral.

Suggestions for Further Work

Any suggestion for future work must really be confined to the fundamental study, so that general effects can be observed and explained in terms of known parameters, such as crystal structures. The non-uniformity of natural ores prevent such investigation.

The brannerite synthesised during the present study proved to be very porous, which led to anomalous results under certain circumstances (e.g. particle size effects on leaching). A fully dense material would have been preferable for leaching studies. Any renewed interest in fundamental brannerite leaching should really start with further investigation of a mode of manufacture by melting techniques.

The influence of iron as a dopant has been investigated. This involved the addition of an ion of one oxidation state lower than the ion it replaced (U(IV)). Calcium, which is reported to occur in brannerite, is bi-valent. Calcium's individual effect and its effect in combination with Fe, on brannerite leachability, might prove interesting. The effect of high-valency ion additions could also be reviewed.

Linked to doping additions is the semi-conductor effect. This could provide useful information on possible leaching mechanisms, but is very much dependent on the production of a fully dense mineral.

Recent trends in leaching studies have been to look at the mechanisms in terms of electrochemical reactions.

The experimental work performed during the course of this project indicated that high oxidant levels were required, and the E_a values suggest some influence of chemical control. A detailed investigation, into the possibility of brannerite dissolution occurring by an electrochemical mechanism, could be undertaken.

It has been possible to partially imitate the chemical composition of natural brannerite by the use of doping elements. However, natural brannerite also has the properties of weathering and being metamict. Attempts could be made to artificially weather the mineral by, for example, high temperature accelerated oxidation. Metamictisation, or lattice disruption, might be simulated by alpha particle bombardment of the mineral. A study could then be made of the two roles, in changing brannerite leaching characteristics.

Table 3, Typical sieve analyses of crushed, synthetic brannerites				
Sieve size	Type of brannerite			
(microns)	Pure	2 ^W /O-Fe ₂ O ₃	3 ^W /O-Fe ₂ O ₃	5 ^W /O-Fe ₂ O ₃
-180+125	5.65%	6.31%	2.87%	3.33%
-125+90	7.62%	16.89%	16.10%	11.74%
-90+63	16.55%	24.91%	30.49%	20.49%
-63+53	8.23%	8.43%	9.94%	8.24%
-53+45	15.66%	13.28%	13.22%	16.90%
-45+38	9.86%	5.53%	5.10%	4.48%
-38	36.44%	24.66%	22.30%	34.80%

Table 4 Diffraction pattern of UO_2 used for synthesis						
Measured d-spacing $\text{\AA}$	Relative Intensity (estimated)	Accurately measured $d_{\text{line}} - d_{\infty}$ X/mm	Calculated d-spacing $\text{\AA}$	Standard Pattern	Standard Pattern d-spacing $\text{\AA}$	Standard Pattern Intensity
7.35	vw	28.25	7.300			
6.30	vw	32.75	6.300			
5.475	vw	37.95	5.443			
3.85	vw	53.8	3.857			
3.295	vw	63.4	3.285			
3.15	vs	66.2	3.150	5-0550	3.157	100
2.735	s	76.8	2.728	5-0550	2.735	48
2.505	vw	84.1	2.501			
2.44	vw	86.6	2.432			
2.23	vw	95.2	2.223			
1.938	s	110.8	1.930	5-0550	1.934	49
1.845	vw	116.5	1.843			
1.644	s	132.1	1.646	5-0550	1.649	47
1.575	m	138.8	1.576	5-0550	1.579	13

Table 5 Diffraction pattern of TiO ₂ used for synthesis						
Measured d-spacing Å	Relative Intensity (estimated)	Accurately measured $d_{line}^{-d_{\infty}}$ Å/mm	Calculated d-spacing Å	Standard Pattern	Standard Pattern d-spacing Å	Standard Pattern Intensity
4.05	vw	51.7	4.011			
3.90	vw	53.5	3.879			
3.505	m	59.45	3.498	23-1446 21-1236 21-1272	3.50 3.50 3.52	80 60 100
3.24	vs	64.5	3.230	21-1276	3.25	100
3.13	vw	66.6	3.130			
2.48	vs	84.95	2.477	21-1276	2.487	50
2.375	vw	88.85	2.373	21-1272	2.378	20
2.33	vw	91.2	2.315	23-1446	2.28	10
2.285	vw	92.35	2.288	21-1276	2.297	8
2.18	mw	96.25	2.200	21-1276	2.188	25
2.12	w	101.1	2.101	23-1446	2.12	60
2.048	vw	104.05	2.046	21-1276	2.054	10
2.00	vw	106.8	1.997	21-1236	1.996	60
1.97	vw	109.0	1.959			
1.93	vw	111.4	1.920			
1.888	vw	113.75	1.884	21-1272	1.892	35
1.690	mw	128.35	1.687	21-1276	1.6874	60
1.678	s	129.4	1.676	23-1446	1.668	80
1.659	vw	130.85	1.660	21-1236	1.663	100
1.619	mw	134.65	1.618	21-1276	1.6237	20
1.473	m	150.2	1.472	21-1276	1.4797	10
1.440	ms	153.7	1.443			

Table 6 Diffraction pattern of Fe_2O_3 used for synthesis						
Measured d-spacing $\text{\AA}$	Relative Intensity (estimated)	Accurately Measured $d_{\text{line}} - d_{\infty}$ X/mm	Calculated d-spacing $\text{\AA}$	Standard Pattern	Standard Pattern d-spacing $\text{\AA}$	Standard Pattern Intensity
3.67	s	56.7	3.664	24-72	3.686	33
3.02	vw	69.2	3.017			
2.68	vs	77.9	2.691	24-72	2.703	100
2.51	vs	83.7	2.512	24-72	2.519	70
2.28	vw	92.5	2.284			
2.195	s	96.3	2.199	24-72	2.208	17
2.07	w	102.7	2.071	24-72	2.080	2
1.835	s	117.0	1.836	24-72	1.843	31
1.685	vs	128.2	1.690	24-72	1.6966	36
1.625	w	133.4	1.632			
1.59	m	136.9	1.595	24-72	1.601	8
1.48	s	149.0	1.482	24-72	1.487	22
1.447	s	153.0	1.449	24-72	1.454	21
1.408	vw	158.0	1.410			

Table 7. Diffraction pattern of "Sellotape" used to mount samples						
Measured d-spacing $\text{\AA}$	Relative Intensity (estimated)	Accurately measured $d_{\text{line}} - d_{\infty}$ X/mm	Calculated d-spacing $\text{\AA}$	Standard Pattern	Standard Pattern d-spacing $\text{\AA}$	Standard Pattern Intensity
4.4	w	46.9	4.415	NO STANDARD PATTERN FOR SELLOTAPE		
3.75	w	55.4	3.748			
3.039	m	68.68	3.039			
3.01	m	69.1	3.021			
2.70	w	73.0	2.865			
2.54	w	83.0	2.532			
2.13	mw	99.9	2.125			
2.09	w	101.6	2.091			
1.99	vw	106.8	1.997			
1.90	w	112.6	1.901			
1.86	w	115.3	1.861			
1.507	vw	146.0	1.508			
1.450	vw	152.7	1.451			

Table 8 Diffraction pattern of pure brannerite sinter						
Measured d-spacing $\text{\AA}$	Relative Intensity (estimated)	Accurately measured $d_{\text{line}} - d_{\infty}$ X/mm	Calculated d-spacing $\text{\AA}$	Standard Pattern	Standard Pattern d-spacing $\text{\AA}$	Standard Pattern Intensity
6.07	s	34.2	6.035	8-2/12-477	6.07/6.04	30/35
4.75	vs	43.6	4.745	8-2/12-477	4.70/4.74	50/95
4.28	s	48.3	4.289	8-2/12-477	4.31/4.29	20/20
3.45	vvs	60.4	3.444	8-2/12-477	3.42/3.44	100/>100
3.355	vs	62.1	3.352	12-477	3.35	>100
3.285	m	63.5	3.280	8-2/12-477	3.32/3.28	60/14
3.025	ms	69.0	3.026	8-2/12-477	3.02	30/35
2.90	ms	72.2	2.896	8-2/12-477	2.91/2.90	50/35
2.775	m	75.5	2.773	8-2/12-477	2.76/2.77	40/30
2.535	m	83.05	2.531	12-477	2.53	30
2.47	m	85.3	2.467	12-477	2.47	30
2.425	m	86.85	2.425	8-2	2.426	20
2.303	vw	91.8	2.301	12-477	2.303	8
2.28	m	92.6	2.282	8-2/12-477	2.276	70/12
2.145	mw	98.95	2.144	8-2/12-477	2.151/2.144	20/10
2.08	mw	102.15	2.081	8-2/12-477	2.080	10/8
2.045	mw	104.1	2.045	12-477	2.043	35
2.015	mw	105.65	2.017	8-2/12-477	2.017/2.015	20/25
1.919	vw	111.3	1.922			
1.90	w	112.6	1.902	8-2/12-477	1.903	80/20
1.8815	mw	113.95	1.881	12-477	1.881	25
1.795	w	119.8	1.797	12-477	1.798	4
1.749	vw	123.4	1.749	12-477	1.749	8
1.720	vw	125.5	1.723	12-477	1.723	4
1.71	w	126.75	1.708	12-477	1.709	20
1.702	mw	127.15	1.703	8-2	1.700	40
1.673	vw	129.5	1.675	12-477	1.672	8
1.639	mw	132.6	1.640	12-477	1.642	8
1.630	vw	133.5	1.631	12-477	1.630	20
1.609	m	135.5	1.610	8-2/12-477	1.609	40/18
1.601	vw	136.7	1.597	12-477	1.597	6
1.576	vw	138.6	1.578	12-477	1.578	10
1.564	vw	140.4	1.560	12-477	1.561	6
1.502	vw	147.4	1.496	12-477	1.493	2
1.489	vw	148.7	1.484	8-2/12-477	1.489/1.486	10/4
1.450	vw	153.2	1.447	12-477	1.450	4
1.428	vw	155.6	1.428			*
1.409	vw	157.8	1.412	8-2	1.411	8
1.383	vw	161.6	1.384			*
1.375	vw	162.5	1.377	8-2	1.371	45
*no further 12-477 listing						

Table 9 Diffraction patterns of pure and doped brannerites; d-spacings					
Pure Brannerite λ	Intensity	² W/O-Fe ₂ O ₃ Brannerite λ	³ W/O-Fe ₂ O ₃ Brannerite λ	⁵ W/O-Fe ₂ O ₃ Brannerite λ	Trend
6.035	s	6.035	6.00	5.98	decrease
4.745	vs	4.745	4.745	4.745	no change
4.289	s	4.289	4.289	4.289	"
3.444	vvs	3.444	3.433	3.422	decrease
3.352	vs	3.342	3.331	3.326	"
3.280	m	3.275	3.265	3.255	"
3.026	ms	3.017	3.004	2.996	"
2.896	ms	2.899	2.896	2.892	no change
2.773	m	2.770	2.759	2.752	decrease
2.531	m	2.524	2.515	2.506	"
2.467	m	2.467	2.489	2.498	increase
	vw		2.464	2.462	appears, +
2.425	m	2.429	2.429	2.429	no change
2.301	vw	2.289	2.287	2.287	decrease
2.282	m	2.282	2.282	2.282	no change
2.144	mw	2.149	2.149	2.144	"
2.081	mw	2.076	2.072	2.065	decrease
2.045	mw	2.041	2.037	2.034	"
2.017	mw	2.011	2.004	1.995	"
1.922	vw	1.917	1.912	1.906	"
1.902	w	1.903	1.898	1.897	no change
	vw			1.890	appears
1.881	mw	1.877	1.873	1.867	decrease
1.797	w	1.791	1.789	1.782	"
1.749	vw	1.747	1.742	1.737	"
1.723	vw	1.723	1.717	1.711	"
1.708	w				disappears
1.703	mw	1.705	1.703	1.705	no change
	vw		1.696	1.688	appears, +
	vw	1.687	1.682	1.681	"
1.675	vw	1.674	1.667	1.662	decrease
1.640	mw	1.636	1.634	1.626	"
1.631	vw	1.628	1.625	1.623	"
1.610	m	1.604	1.600		disappears, +
1.597	vw	1.597	1.589	1.597	no change
	vw		1.580	1.578	appears, +
1.578	vw	1.576	1.572	1.567	decrease
1.560	vw				disappears
	vw			1.545	appears
1.496	vw	1.496	1.496	1.496	no change
1.484	vw				disappears
1.447	vw	1.442	1.447	1.450	no change
1.428	vw	1.428	1.431	1.431	"
1.412	vw	1.408	1.412	1.412	"
1.385	vw	1.382	1.380	1.375	decrease
1.377	vw	1.366	1.367	1.364	decrease

Table 10 Effect of sulphuric acid concentration on leaching pure brannerite						
Leaching Conditions 75°C, under air, no oxidant, 1000 rpm, 1 gm solid, 200ml solution						
Variable →	100 g/l H ₂ SO ₄		200 g/l H ₂ SO ₄		500 g/l H ₂ SO ₄	
Time/hours↓	% U	% Ti	% U	% Ti	% U	% Ti
0.5	0.035	0.873	0.036	0.839	0.027	0.113
1	0.040	0.888	0.049	0.866	0.046	0.201
2	0.049	0.897	0.071	0.888	0.074	0.209
4	0.061	0.950	0.079	0.917		
5					0.161	0.356
8	0.093	1.010	0.097	0.920	0.258	0.422
22	0.174	1.072	0.179	0.974		
24					0.729	0.600
25	0.180	1.078	0.203	1.027		
28	0.194	1.107	0.212	1.029	0.851	0.714
32					0.976	0.735
	Ti:U mole ratio		Ti:U mole ratio		Ti:U mole ratio	
0.5	50.366		46.003		8.239	
1	44.298		35.390		8.696	
2	36.387		25.212		5.634	
4	30.956		23.085			
5					4.796	
8	21.688		19.006		3.278	
22	12.418		10.903			
24					1.663	
25	11.889		10.111			
28	11.410		9.718		1.677	
32					1.506	

Table 11 Effect of oxidant addition on sulphuric acid leaching of pure brannerite.														
Leaching Conditions 75°C, under air, 100 g/l H ₂ SO ₄ , 1000 rpm, 1 gm solid, 200 ml solution														
Variable	no oxidant		under O ₂ gas		H ₂ O ₂ single addition		H ₂ O ₂ stepwise		H ₂ SO ₅ single addition		H ₂ SO ₅ stepwise		10 g/l Fe ³⁺	
Time/ hours	% U	% Ti	% U	% Ti	% U	% Ti	% U	% Ti	% U	% Ti	% U	% Ti	% U	% Ti
0.5	.035	.873	.047	.895	3.097	2.209	2.532	2.487	1.148	2.557	1.032	2.000	2.222	1.920
1	.040	.888	.055	.905	4.333	3.334	4.012	3.613	2.178	3.699	1.601	2.850	2.959	2.521
2	.049	.897	.075	.911	5.711	4.971	7.051	6.358	3.298	4.288	2.422	3.324	3.858	2.958
4	.061	.950	.083	.956	8.022	7.821	8.821	9.799	3.941	4.654	3.117	3.956	5.248	4.569
8	.093	1.010	.115	.979	12.926	13.344	14.339	16.443	4.576	5.135	3.882	4.769	7.406	6.961
21			.195	1.104										
22	.174	1.072			23.159	18.729	25.602	27.963						
24									5.502	5.976	5.087	5.848	12.479	12.042
25	.180	1.078	.228	1.168					5.552	6.265	5.321	6.088		
26														
27					24.918	19.912	28.401	30.205						
28	.194	1.107											13.575	12.456
29			.261	1.353	25.245	20.268	29.223	31.296						
29.5									5.673	-	5.682	-		
32													14.502	13.104
	Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio	
0.5	50.366		37.984		1.427		1.964		4.453		3.877		1.728	
1	44.298		32.632		1.539		1.801		3.401		3.561		1.703	
2	36.387		24.320		1.741		1.804		2.601		2.274		1.533	
4	30.956		23.161		1.950		2.222		2.362		2.538		1.741	
8	21.688		16.969		2.065		2.294		2.244		2.457		1.880	
21			11.324											
22	12.418				1.617		2.184							
24									2.103		2.299		1.930	
25	11.889		11.872						2.257		2.289			
26														
27					1.598		2.127							
28	11.410												1.835	
29			8.945		1.606		2.142							
29.5									-		-			
32													1.807	

Table 12 Effect of varying oxidant (Fe^{3+}) concentration on 100 g/l H_2SO_4 leaching of pure brannerite										
Leaching Conditions 75°C , under air, 100 g/l H_2SO_4 , 1000rpm, 1 gm solid, 200 ml solution										
Variable	1 g/l Fe^{3+}		2.5 g/l Fe^{3+}		5 g/l Fe^{3+}		10 g/l Fe^{3+}		15 g/l Fe^{3+}	
Time/hours	% U	% Ti	%U	% Ti	% U	% Ti	% U	% Ti	% U	% Ti
0.5	1.327	.770	2.152	.818	2.179	1.226	2.222	1.920	2.751	1.925
1	2.032	1.331	2.789	1.436	2.943	1.884	2.959	2.521	3.290	3.151
2	3.105	2.172	3.552	2.228	3.749	2.386	3.858	2.958	4.562	4.047
4	4.286	3.371	4.765	3.736	4.816	3.820	5.248	4.569	5.404	5.038
8	5.815	5.250	6.708	6.045	6.884	6.257	7.406	6.961	7.476	7.514
20	8.207	7.748								
24			10.703	11.607	12.243	11.750	12.479	12.042	12.902	12.464
25	8.832	8.508								
27									13.664	12.920
28			11.354	12.018	12.590	12.453	13.575	12.456		
30	9.355	8.972							14.390	13.726
31					12.706	12.981				
32			11.817	12.582			14.502	13.104		
	Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio	
0.5	1.161		.761		1.125		1.728		1.399	
1	1.311		1.029		1.280		1.703		1.916	
2	1.399		1.288		1.273		1.533		1.774	
4	1.573		1.568		1.586		1.741		1.865	
8	1.806		1.802		1.817		1.880		2.010	
20	1.888									
24			2.169		1.919		1.930		1.932	
25	1.927									
27									1.894	
28			2.117		1.978		1.835			
30	1.918								1.908	
31					2.043					
32			2.130				1.807			

Table 13(a) Effect of temperature on leaching pure brannerite in 100 g/l H_2SO_4 containing 10 g/l Fe^{3+}

Leaching Conditions under air, 100 g/l H_2SO_4 , 10 g/l Fe^{3+} , 1000 rpm, 1 gm solid, 200 ml solution								
Variable→ Time/hours ↓	30.5°C,%U	40.3°C,%U	50.6°C,%U	58.5°C,%U	66.0°C,%U	75.5°C,%U	80.0°C,%U	96.7°C,%U
0.5	.981	1.339	2.298	3.620	4.338	4.998	6.245	7.316
1	1.354	2.142	3.459	5.066	5.687	5.976	6.644	8.619
2	1.906	2.900	4.963	6.016	6.196	6.600	7.477	10.540
4	2.684	4.075	5.909	6.333	6.622	7.315	8.876	12.879
8	3.825	5.250	6.252	6.764	7.353	8.120	10.858	16.252
24	5.731	6.337	6.974	8.264	9.157	11.615	15.994	23.171
27	5.859		7.071		9.443			24.287
27.5				8.661				
28		6.484				12.622	17.167	
30	6.004	6.679	7.205		9.740			25.310
31				9.343				
32						13.531	18.026	
Variable→ Time/hours ↓	30.5°C,%Ti	40.3°C,%Ti	50.6°C,%Ti	58.5°C,%Ti	66.0°C,%Ti	75.5°C,%Ti	80.0°C,%Ti	96.7°C,%Ti
0.5	.097	.098	.110	.128	.188	.486	.613	2.215
1	.106	.139	.163	.218	.226	.836	1.141	3.702
2	.165	.249	.271	.334	.470	1.796	2.259	6.180
4	.179	.282	.342	.485	1.059	3.167	4.096	9.359
8	.300	.308	.701	1.092	1.972	5.082	6.586	13.383
24	.495	.980	1.600	2.915	4.387	8.592	12.575	20.131
27	.499		1.733		4.770			21.301
27.5				3.270				
28		1.177				9.279	13.715	
30	.642	1.293	1.811		5.106			22.480
31				3.568				
32						9.816	14.456	

Table 13(b)		Ti:U mole ratio						
Time/hours	30.5°C	40.3°C	50.6°C	58.5°C	66.0°C	75.5°C	80.0°C	96.7°C
0.5	.198	.146	.096	.071	.086	.194	.196	.606
1	.157	.130	.094	.086	.079	.289	.343	.859
2	.173	.172	.109	.111	.152	.544	.604	1.173
4	.133	.138	.116	.153	.320	.866	.923	1.453
8	.159	.117	.224	.323	.536	1.252	1.213	1.647
24	.173	.309	.459	.706	.958		1.572	1.738
27	.170	.363	.490		1.010	1.479		1.754
27.5				.755				
28						1.470	1.598	
30	.214	.387	.503		1.048			1.776
31				.764				
32						1.450	1.604	

Table 13(c) 5% Extraction, Measured rates, Graphs 4(a),4(b)						Calculated E_a , Graphs 4(c),4(d),4(e)		
Temperature/ $^{\circ}\text{C}$	$\frac{1}{T} \times 10^3, \text{K}^{-1}$	U rate/ hr^{-1}	Ti rate/ hr^{-1}	U,ln rate	Ti,ln rate	Temperature/ $^{\circ}\text{C}$	U, E_a/kJmole^{-1}	Ti, E_a/kJmole^{-1}
30.5	3.295	.10616	.01622	-2.2428	-4.1215	30	136.673	40.186
40.3	3.192	.24444	.03836	-1.4088	-3.2607	40	98.784	46.075
50.6	3.090	.86250	.05866	-0.1479	-2.8360	50	83.673	61.664
58.5	3.017	1.69231	.11460	0.5261	-2.1663	60	65.271	65.129
66.0	2.950	3.53571	.16850	1.2629	-1.7835	70	52.555	81.064
75.5	2.869	4.32340	.40750	1.4640	-0.8977	80	44.254	85.499
80.0	2.833	4.61538	.68390	1.5294	-0.3799	90	36.149	99.079
96.7	2.705	10.86957	2.43420	2.3860	0.8896			

Table 14 Effect of particle size on leaching pure brannerite in 10 g/l Fe ³⁺ /100 g/l H ₂ SO ₄						
Leaching Conditions 75°C, under air, 100 g/l H ₂ SO ₄ + 10 g/l Fe ³⁺ , 1000 rpm, 1 gm solid, 200 ml solution						
Variable	-180+125 μm	-125+90 μm	-90+63 μm	-63+53 μm	-53+45 μm	-38μm
Time/hours	%U	%U	%U	%U	%U	%U
0.5	10.468	8.374	5.679	5.313	4.528	4.409
1	11.613	9.970	6.953	5.747	5.251	5.087
2	12.034	10.483	7.521	6.461	5.763	5.713
4	13.074	11.225	8.139	7.764	6.908	6.420
8	14.625	12.565	10.140	9.905	8.666	7.678
23		17.795				
24	19.474		15.474	15.384	14.888	12.285
27	20.508		16.424	16.385	15.640	13.423
27.5		19.019				
30	21.377	19.820	17.330		16.018	15.109
31.5				17.660		

Table 15 Effect of leaching pure brannerite in inorganic acids of molarity equivalent to 1 molar H ₂ SO ₄								
Leaching Conditions 75°C, under air, no oxidant, 1000 rpm, 1 gm solid, 200 ml solution								
Variable	0.5 M H ₂ SO ₄		1.0 M H ₂ SO ₄		Equivalent HCl		Equivalent HNO ₃	
Time/hours	%U	%Ti	%U	%Ti	%U	%Ti	%U	%Ti
0.5	.076	.050	.140	.050	.107	.049	.100	.048
1	.102	.056	.161	.068	.139	.053	.184	.097
2	.143	.074	.175	.086	.163	.100	.282	.178
3	.150	.079	.196	.095	.196	.145	.372	.185
4	.173	.081	.202	.095	.210	.145	.464	.226
5	.190	.087	.220	.124	.211	.171	.500	.243
6	.196	.094	.226	.133	.230	.176	.628	.331
8	.223	.111	.241	.133	.268	.184	1.557	.548
10	.240	.112	.252	.169	.282	.224	2.406	.891
Time/hours	Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio	
0.5	1.319		.719		.914		.948	
1	1.088		.839		.758		1.053	
2	1.034		.979		1.230		1.261	
3	1.048		.968		1.480		.997	
4	.936		.942		1.387		.973	
5	.920		1.126		1.620		.970	
6	.958		1.172		1.532		1.055	
8	.991		1.101		1.367		.703	
10	.930		1.293		1.591		.741	

Table 16 Effect of leaching pure brannerite in ferric iron-containing inorganic acids of molarity equivalent to 1 molar H_2SO_4

Leaching Conditions 75°C , under air, 1000 rpm, 1 gm solid, 200 ml solution

Variable	0.5 M H_2SO_4 +10g/l Fe^{3+}		1.0M H_2SO_4 +10g/l Fe^{3+}		equivalent HCl+10g/l Fe^{3+}		equivalent HNO_3 + 10g/l Fe^{3+}	
Time/hours	%U	%Ti	%U	%Ti	%U	%Ti	%U	%Ti
0.5	3.860	.143	3.905	.455	3.261	.358	2.426	.328
1	4.479	.279	4.783	.643	4.402	.562	3.626	.864
2	4.672	.423	5.305	1.152	5.044	.814	5.133	1.854
3	4.875	.591	5.678	1.692	5.424	1.134	6.200	2.689
4	5.001	.734	6.077	2.102	5.665	1.438	6.974	3.383
5	5.094	.858	6.452	2.581	6.049	1.767	7.638	3.994
6	5.293	1.068	6.782	2.897	6.358	2.078	8.149	4.681
8	5.681	1.398	7.475	3.687	6.882	2.560	9.335	6.069
10	5.880	1.593	7.875	4.098	7.241	2.892	10.299	6.957
Time/hours	Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio	
0.5	.0739		.2330		.2196		.2707	
1	.1246		.2690		.2552		.4763	
2	.1813		.4343		.3226		.7226	
3	.2426		.5960		.4181		.8673	
4	.2936		.6918		.5078		.9700	
5	.3369		.8002		.5841		1.0459	
6	.4035		.8542		.6537		1.1488	
8	.4921		.9867		.7440		1.3002	
10	.5418		1.0408		.7989		1.3511	

Table 17 Effect of leaching pure brannerite in sulphuric acid of varying concentration with constant oxidant level, 10 g/l Fe ³⁺						
Leaching Conditions 75°C, under air, 1000 rpm, 1 gm solid, 200 ml solution						
Variable	0.5M H ₂ SO ₄ + 10g/l Fe ³⁺		1.0M H ₂ SO ₄ + 10g/l Fe ³⁺		2.0M H ₂ SO ₄ + 10g/l Fe ³⁺	
Time/hours	%U	%Ti	%U	%Ti	%U	%Ti
0.5	3.860	.143	3.905	.455	4.059	.803
1	4.479	.279	4.783	.643	4.937	1.288
2	4.672	.423	5.305	1.152	6.130	2.252
3	4.875	.591	5.678	1.692	6.644	2.839
4	5.001	.734	6.077	2.102	7.286	3.504
5	5.094	.858	6.452	2.581	7.918	4.203
6	5.293	1.068	6.782	2.897	8.408	4.765
8	5.681	1.398	7.475	3.687	9.383	5.856
10	5.880	1.593	7.875	4.098	10.179	6.808
Time/hours	Ti:U ratio		Ti:U ratio		Ti:U ratio	
0.5	.0739		.2330		.3957	
1	.1246		.2690		.5218	
2	.1813		.4343		.7349	
3	.2426		.5960		.8546	
4	.2936		.6918		.9620	
5	.3369		.8002		1.0617	
6	.4035		.8542		1.1333	
8	.4921		.9867		1.2483	
10	.5418		1.0408		1.3378	

Table 18 Effect of acid-baking pure brannerite on leaching characteristics						
Leaching Conditions Pure brannerite baked at 150°C, for 24 hours, in 50 ^w /o H ₂ SO ₄ . Leach:75°C, under air, 1000 rpm, 1 gm solid, 200 ml solution						
Variable	Acid bake, Water leach		Acid bake, 100 g/l H ₂ SO ₄ leach		Acid bake, 100 g/l H ₂ SO ₄ + 10 g/l Fe ³⁺ leach	
Time/hours	%U	%Ti	%U	%Ti	%U	%Ti
0	53.370	61.384	53.345	61.355	53.381	61.386
0.5	58.153	64.850	58.803	65.204	59.625	66.048
1	58.474	65.091	58.880	65.372	60.301	66.513
2	58.715	65.394	58.998	65.620	61.197	66.821
4	58.789	65.611	59.031	65.902	63.200	67.666
8			59.507	66.283	65.942	68.610
8.25	58.857	65.725				
21	59.177	67.392				
24			59.710	67.987	68.148	72.244
25	59.466	67.436				
27			59.733	68.661	68.379	72.807
29	59.623	67.623				
30			59.893	68.705	68.402	73.559
Time/hours	Ti:U ratio		Ti:U ratio		Ti:U ratio	
0	2.300		2.300		2.300	
0.5	2.230		2.218		2.215	
1	2.226		2.221		2.206	
2	2.227		2.224		2.184	
4	2.232		2.233		2.141	
8			2.228		2.081	
8.25	2.233					
21	2.278					
24			2.277		2.120	
25	2.268					
27			2.299		2.130	
29	2.275					
30			2.294		2.151	

Table 19 Effect of Fe_2O_3 -doping on leachability of brannerite in 100 g/l H_2SO_4 , with stoichiometric H_2O_2 addition for U(IV) to U(VI) oxidation

Leaching Conditions 75°C , 100 g/l H_2SO_4 , stoichiometric H_2O_2 for U(IV) to U(VI) oxidation, under air, 1000 rpm, 1 gm solid, 200 ml solution

Variable	Pure brannerite		$2^{\text{W}}/\text{oFe}_2\text{O}_3$ -brannerite		$3^{\text{W}}/\text{oFe}_2\text{O}_3$ -brannerite		$5^{\text{W}}/\text{oFe}_2\text{O}_3$ -brannerite	
Time/hours	%U	%Ti	%U	%Ti	%U	%Ti	%U	%Ti
0.5	.645	2.135	.530	1.986	.280	1.600	.095	1.529
1	1.941	2.209	1.197	2.152	.986	2.050	.528	2.010
2	4.440	3.028	1.969	2.704	1.887	2.685	1.332	2.580
4	6.351	5.449	3.742	4.336	3.603	3.930	2.494	3.508
8	8.938	10.219	7.127	7.879	6.966	6.489	4.935	5.938
24	14.495	16.000	10.464	10.460	9.259	10.019	7.036	8.272
28	15.077	16.408	10.905	10.500	9.450	10.128	7.287	8.585
32	15.134	16.495	11.310	10.946	9.843	10.386	7.691	8.740
Time/hours	Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio	
0.5	6.6175		7.8660		11.7916		34.9307	
1	2.2770		3.7140		4.3671		8.2805	
2	1.3643		2.8362		2.9887		4.2073	
4	1.7155		2.3937		2.2913		3.0559	
8	2.2867		2.2839		1.9565		2.6148	
24	2.2076		2.0995		2.2353		2.5545	
28	2.1766		2.0220		2.2140		2.5599	
32	2.1799		2.0327		2.1797		2.4693	

Table 20 Effect of Fe_2O_3 -doping on leachability of brannerite in 100 g/l H_2SO_4 + 10 g/l Fe^{3+} (as excess oxidant)

Leaching Conditions 100 g/l H_2SO_4 + 10 g/l Fe^{3+} , 75°C, under air, 1000 rpm, 1 gm solid, 200 ml solution

Variable	Pure brannerite		$2^{\text{W}}/\text{oFe}_2\text{O}_3$ -brannerite		$3^{\text{W}}/\text{oFe}_2\text{O}_3$ -brannerite		$5^{\text{W}}/\text{oFe}_2\text{O}_3$ -brannerite	
Time/hours	%U	%Ti	%U	%Ti	%U	%Ti	%U	%Ti
0.5	3.524	.463	2.225	.256	1.892	.199	1.642	.096
1	4.553	.819	2.885	.438	2.093	.282	1.963	.212
2	5.028	1.511	3.154	.685	2.343	.488	2.131	.365
3	5.595	1.907	3.343	.982	2.660	.684	2.281	.555
4	5.957	2.352	3.557	1.245	2.829	.934	2.433	.693
5	6.527	3.110	3.745	1.531	3.125	1.129	2.606	.867
6	6.938	3.629	3.970	1.741	3.323	1.298	2.735	.969
8	7.652	4.249	4.332	2.086	3.670	1.708	2.986	1.246
10	8.262	5.066	4.714	2.414	3.970	2.092	3.226	1.453
Time/hours	Ti:U ratio		Ti:U ratio		Ti:U ratio		Ti:U ratio	
0.5	.263		.242		.217		.127	
1	.360		.319		.278		.234	
2	.601		.456		.431		.372	
3	.681		.617		.531		.529	
4	.789		.735		.682		.619	
5	.953		.858		.747		.723	
6	1.046		.921		.807		.770	
8	1.111		1.011		.962		.907	
10	1.226		1.076		1.089		.977	

Table 21 Effect of leaching Rio Algom brannerite ore under various conditions

Leaching Conditions Under air, 1000 rpm, 20 gm ore, 200 ml solution

Variable	10% H_2SO_4 75°C	100g/l H_2SO_4 75°C	Pre-bake with w/w H_2SO_4 , 100g/l H_2SO_4 leach, 75°C	Distilled water 25°C	10g/l H_2SO_4 25°C	25g/l H_2SO_4 25°C	50g/l H_2SO_4 25°C	100g/l H_2SO_4 25°C	200g/l H_2SO_4 25°C
Time/hours	%U	%U	%U	%U	%U	%U	%U	%U	%U
1	96.51	74.28	98.50	0.27	18.22	26.43	29.80	35.26	40.63
2	97.36	83.88	94.12	0.08	23.61	33.34	37.55	42.50	47.91
3	96.79	91.09	94.58	0.14	27.38	37.91	43.45	46.58	52.37
4	97.33	95.33	94.58	0.14	30.93	41.45	45.49	49.54	55.35
5	97.43	98.05	94.78	0.14	34.07	43.88	47.63	51.25	57.78
6	97.81	99.73	94.50	0.14	36.90	45.86	50.74	53.95	59.12
Residue Analysis %U	0.002	0.0025	0.0006	.049	.036	-	.030	.028	-

Table 22 Effect of various oxidants on the leaching of natural brannerite ore (Rio Algom) at 75°C with 50 g/l H ₂ SO ₄								
Leaching Conditions 50 g/l H ₂ SO ₄ , 75°C, under air (except where stated), 1000 rpm, 20 gm ore, 200 ml solution								
Variable	Control no oxidant	H ₂ SO ₅ added at start	H ₂ SO ₅ added at times*	H ₂ O ₂ added at start	H ₂ O ₂ added at times*	KClO ₃ added at start	MnO ₂ added at start	Leach under oxygen
Time/hours	Uranium Extraction: mg per 20 gm sample of ore							
0	0	0	0*	0	0*	0	0	0
0.5	10.098	10.205	9.927	11.227	10.033	10.411	11.049	11.850
1	11.190	11.126	10.988	12.127	11.148	11.407	12.013	14.093
2	12.493	12.981	12.194*	13.444	12.485*	13.252	13.346	15.903
4	14.377	15.472	16.005*	16.286	15.934*	15.792	15.563	16.892
8	16.590	16.247	16.424*	17.195	16.792*	16.557	16.314	17.227
22	16.914	16.657	16.690*	17.609	17.123*	16.912	16.654	17.896
27			16.678*					
28	17.076	16.774		17.859	17.213*	17.054	16.839	18.235
31			16.818					
32	17.263	16.955		17.956	17.487	17.156	16.940	18.683
Residue Analysis %U	0.0018	0.0010	0.0009	0.0009	-	0.0010	0.0014	-

APPENDIX 2GLOSSARY OF GEOLOGICAL TERMS

Conchoidal Fracture - a type of rock or mineral fracture giving smoothly curved surfaces. Characteristic of quartz.

Detrital - said of minerals occurring in sedimentary rocks which were derived, as gravels, from pre-existing igneous, sedimentary or metamorphic rocks. Hard or heavy minerals are often found in detrital deposits.

Dike - a tabular body (thin sheet) of igneous rock that cuts across the structure of adjacent rocks, or cuts massive rocks, more or less vertically. Although most dikes result from the intrusion of magma, some are the result of metasomatic replacement.

Diorite - a plutonic rock. Small amounts of quartz may be present.

Isometric (crystallographically) - that system of crystals in which the forms are referred to by three equal, mutually perpendicular, axes.

Isotropic - having the same properties in all directions; most commonly used for optical properties. Typical of amorphous substances and of crystals of the isometric system. Contrasts with anisotropic.

Magma - naturally occurring, mobile rock material (molten) generated within the earth and capable of intrusion and extrusion. The material from which igneous rocks are thought to have been derived, by solidification and related processes.

Magmatic (adj.) - changes in rocks and minerals that form as a result of magma movement.

Metamict - a mineral, containing radioactive elements, in which varied degrees of lattice disruption have taken place as a result of radiation damage while, at the same time, retaining the original external morphology.

Metamorphic Rock - includes all those rocks which have formed in the solid state in response to pronounced changes of temperature, pressure and chemical environment, which take place (in general) below the shells of weathering and cementation.

Paramorph - a pseudomorph that is chemically identical with the original crystal, but the atoms have been re-arranged so that they no longer conform to the original outline.

Pegmatite - a very coarse granite; usually forms dikes that cut granite or the gneisses and shists that border granite masses. Pegmatites represent the last liquid portion of the crystallising granite magma. They are coarse because the liquid residue, at the time of crystallisation, contained a high percentage of water and other volatile elements that did not go into the make-up of the common minerals of granite. They were, for that reason, concentrated in the residue. They are interesting mineralogically because minerals of the rarer elements are found with the coarser quartz, feldspar and mica that principally compose them.

Placer - a deposit of heavy minerals in stream beds, in which the valuable substances have been concentrated as the lighter weight minerals have been carried away by the stream. Typically used to describe the place where gold is found as a result of washing gold-bearing alluvial or glacial deposits.

Pseudomorph - a crystal or apparent crystal having the outward form of another species of mineral which it has replaced, by substitution or by chemical alteration. It may form by a breakdown and rearrangement of the same atoms (a paramorph), by a slight change in composition, by a coating over another crystal or by a complete replacement by an entirely different mineral.

All definitions taken from reference (58).

APPENDIX 3

THE CALCULATION AND CONSTRUCTION OF AN E_H -pH DIAGRAM FOR THE SYSTEM Fe-Ni-S- H_2O , INCLUDING PENTLANDITE (Fe,Ni_9S_8), AT 25°C.

Introduction

Hydrometallurgical processes are principally concerned with kinetics, rather than thermodynamic considerations, by virtue of the relatively low temperatures of operation. Nevertheless, thermodynamic data, applied to hydrometallurgy, give an indication of the stable solid and dissolved species which might be expected, under specific operating conditions.

The E_H -pH diagram is a convenient method of predicting which species, in a metal/compound/water system, should be formed, from thermodynamic considerations, under particular conditions of oxidation potential (a measure of electron activity) and pH (a measure of proton activity).

The principles underlying the calculation and construction of an E_H -pH diagram, at 25°C, are well known, and so are only briefly indicated below. More stringent accounts of the theory are widely given in references ((54), (62), (63) and (71) are typical).

The standard free energy change of a reaction, involving species under consideration, is found from the relationship:

$$\Delta G_{298}^O(\text{reaction}) = \Sigma G_{298}^O(\text{products}) - \Sigma G_{298}^O(\text{reactants})$$

The free energies of the components, G_{298}^O , are listed in Appendix A3.A1, the values having been taken from numerous, well-established, sources.

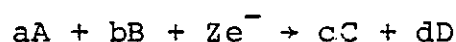
The reactions under consideration are typically written as half-cell reactions, since any reaction in an aqueous system can be written in terms of electron addition/removal, H^+ addition/removal or a combination of the two.

For non-redox reactions, the relation between standard free energy change and equilibrium constant can be written:

$$\ln k = - \frac{\Delta G_{298}^O}{RT},$$

which can then be expanded to a relationship between pH and the activities of the species involved, to give a line required for the construction of the diagram.

A redox reaction can be written as the half-cell:



for which the half-cell reduction potential, E_T , is given by the Nernst Equation:

$$E_T = E_T^O - \frac{RT}{ZF} \ln \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b} \quad \text{where } \{ \} \text{ indicates activity.}$$

$$\text{Here } E_T^O = - \frac{\Delta G_T^O}{ZF}.$$

For standard conditions of pressure, and temperature = 298.15K, the above Nernst Equation becomes:

$$E_T = \frac{-\Delta G_{298}^O}{96487Z} - \frac{0.05916}{Z} \log \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b},$$

which gives an equation, involving potential and pH, at a line on the E_H -pH diagram.

The thermodynamic stability limits of water are also plotted on the diagram, but often due to kinetic effects, this range is extended slightly.

The use of half-cell reactions is valid at 298K since, by definition of the hydrogen half-cell, $\Delta G_{298}^{\circ} = 0$, $G_{298}^{\circ}(\text{H}_2) = 0$ and $G_{298}^{\circ}(\text{H}^+) = 0$, which implies that $G_{298}^{\circ}(\text{e}^-) = 0$. However, this assumption is not true at elevated temperatures, when the thermodynamic properties of the electron have to be taken into account.^{(59), (71)}

The first major assumption, in the construction of an E_{H} -pH diagram, is that the free energies of formation of all the species are either known, or can be estimated with a high degree of confidence. For a mineral such as brannerite, no data exist. The method described below uses the E_{H} -pH diagram to predict a free energy of formation, for a mineral, based on a rough estimate of what the thermodynamic value might be.

For convenience, a specific Fe-Ni-S- H_2O system was chosen because a complex mineral, pentlandite, exists and an approximate value of $\Delta G_{\text{f}}^{\circ}(\text{pentlandite})$ could be estimated from well-established data. However, the method is equally applicable to brannerite, except that the lack of an approximately accurate estimate of $\Delta G_{\text{f}}^{\circ}(\text{brannerite})$ would necessitate the use of computer iterative methods, to undertake the method described below.

A3.1 Pentlandite

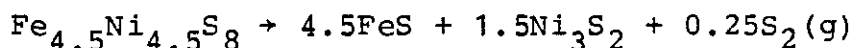
Pentlandite is the most common of the sulphide ore minerals of nickel (accounting for approximately three-quarters of the nickel mined in the world), making it the most important mineral source of nickel. The largest deposits are found in the Sudbury, Ontario region

of Canada and in the Kola Peninsula of the Finland-U.S.S.R. border.

It is rarely found in large crystals or pure masses, it is almost invariably associated with large amounts of pyrrhotite (iron sulphide $\text{FeS} \rightarrow \text{Fe}_7\text{S}_8$) and smaller amounts of nickel sulphides. $(\text{Fe},\text{Ni})_9\text{S}_8$ exists in solid solution or as a fine dispersion in the iron sulphide mass. Extraction of nickel from such deposits is by a mineral processing route, to produce a concentrate, then by hydrometallurgical methods.

The ideal formula of pentlandite is $(\text{Fe},\text{Ni})_9\text{S}_8$ ($\text{Ni} = 34.2\%$). Typically, the Fe:Ni ratio varies from 0.8 to 1.2. In the current exercise, a 1:1 ratio is assumed as an average composition and for ease of manipulation, for diagram construction.

Experimental thermodynamic data for pentlandite are not available, hence a theoretical value for $G_{298}^{\circ}(\text{Fe},\text{Ni})_9\text{S}_8$ was estimated⁽⁶⁴⁾ by considering the decomposition equation:



The process involved extrapolating high temperature data⁽⁷²⁾ back to 298K.

The value estimated was $G_{298}^{\circ}(\text{pentlandite}) = -179.66 \text{ kcal mole}^{-1}$.

Care had to be exercised in using this value as many assumptions were made, the most notable of which were:

- a linear relationship between thermodynamic property and temperature,
- no phase change or transformation occurred in the temperature range considered, although many iron

and nickel sulphides generally do show some degree of transformation on temperature cycling.

A3.2 Species considered for the Diagrams

The species considered for the diagrams fall into several categories:

- (a) the species considered most likely to appear on the diagrams, from published diagrams⁽⁶³⁾ and past experience,
- (b) species for which there are reliable thermodynamic data available or, for which, data could be reliably estimated. Thus, in the system, no account was taken of jarosites or any basic sulphates,
- (c) species of definite chemical composition. No account was taken of any iron sulphide with a composition in the range FeS_{1-2} ,
- (d) species which give the diagrams most meaning and practical use, from an extractive metallurgical viewpoint.

The species considered appear in Appendix A3.A1.

Although $\text{Fe}^{3+}_{(\text{aq})}$ and $\text{HNiO}_2^{-}_{(\text{aq})}$ were considered, they do not appear on the diagrams for the activities investigated. These species would appear on diagrams for which the activities of dissolved and ionic species are considerably less than 10^{-1} (example $<10^{-3}$)⁽⁶³⁾.

A3.3 Construction of Diagrams

A3.3(i) General

E_{H} -pH diagrams were constructed for the following systems:

- (i) $S-H_2O$
- (ii) $Fe-H_2O$,
- (iii) $Ni-H_2O$,
- (iv) $Fe-S-H_2O$,
- (v) $Ni-S-H_2O$,
- (vi) $Fe-Ni-S-H_2O$. See part A3.3(ii)

In drawing the E_H -pH diagrams, certain assumptions were made:

- a) the diagrams were drawn using data valid at 298K (and 1 atmosphere pressure) only; hence the diagrams are valid only at this specific temperature (and pressure).
- b) the activity of neutral and solid species was unity,
i.e. $a_{H_2O} = 1$, $a_{NiS} = 1$, etc.
- c) the activity of dissolved and ionic species was defined as 0.1,
i.e. $a_{Ni^{2+}} = 0.1$, $a_{H_2S} = 0.1$, $a_{SO_4^{2-}} = 0.1$.
- d) the activity of H_2 and O_2 was taken as unity.

The diagrams were drawn in terms of activities rather than concentrations. This simplification was necessary as there is not a reliable method of calculating activity coefficients at the activities used.

The above assumptions limit the validity of the diagrams to the temperature (and pressure) and activities stated above. They only take into account thermodynamic stability; there is no indication of kinetic stability.

The method of construction involved superimposing the simpler diagrams:

Example: $(S-H_2O) + (Fe-H_2O)$ or $(S-H_2O) + (Ni-H_2O)$,
and then, in view of the stable phases present,
determining the regions of stability of the mixed species:

Example: FeS , FeS_2 or NiS , Ni_3S_2 ,
to produce a "three-component" diagram.

Example: $\text{Fe-S-H}_2\text{O}$ or $\text{Ni-S-H}_2\text{O}$.

The "four-component" diagram ($\text{Fe-Ni-S-H}_2\text{O}$) was produced in a similar manner, by superimposing the two "three-component" systems and determining the domain of stability of the mixed sulphide pentlandite, compatible with the stable phases present.

Data used in the calculations are listed in Appendix A3.A1. A reference is given for each value, although most values were cross-checked with other references (notably (60), (61), (63), (65), (66), (67), (68), (69)).

Appendix A3.A2 lists the half-cell reactions involving the relevant species which occurred to produce lines on the diagrams. All of the possible reactions involving the necessary species were considered, during the construction of the diagrams, but those which do not exist on the diagram are omitted for clarity.

Appendix A3.A3 lists the appropriate Nernst Equations (for redox reactions) and simple equilibrium equations (for non-redox reactions), which arose from ΔG_T^0 calculations for the reactions in Appendix A3.A2. These numerical equations are shown in terms of general activities of dissolved and ionic species (although, assumptions (a), (b) and (d) above are still valid).

Appendix A3.A4 lists the numerical equations, taking into account assumptions (a), (b), (c) and (d) outlined above, for plotting on the E_H -pH diagram.

Appendix A3.A5 contains the various diagrams constructed.

Appendix A3.A6 shows the key to the regions of stability occurring on the more complex diagrams.

A3.3(ii) Introduction of Pentlandite

The value of G_{298}^{O} (pentlandite) = -179.66 kcal mole⁻¹ (from reference (64)) resulted in the thermodynamic instability of (Fe,Ni)₉S₈ on the (Fe-Ni-S-H₂O) diagram, under the conditions investigated. It appeared that the mixture of iron and nickel sulphides was more stable than a mixed Fe-Ni sulphide.

However, pentlandite is a mineral widely occurring in nature, especially in combination with iron and nickel sulphides; hence, it might reasonably be expected to exist on the diagram at approximately the same position as the iron and nickel sulphides.

Thus, it was concluded that the theoretical G_{298}^{O} (pentlandite) value from reference (64) was not sufficiently negative, to allow a domain of stability to exist on the Pourbaix Diagram.

A range of G_{298}^{O} (pentlandite) values down to -300 kcal mole⁻¹ was considered to investigate the resulting regions of stability of (Fe,Ni)₉S₈ on the (Fe-Ni-S-H₂O) diagram.

The half-cell and numerical equations that arose are listed in Appendices A3.A2, A3.A3 and A3.A4.

The regions of stability of pentlandite, for the chosen values of G_{298}^{O} , are shown in Diagram A3.7. The domains of stability are those consistent with the species existing on the "four-component" diagram (Fe-Ni-S-H₂O), although the remainder of the diagram is omitted for clarity. Pentlandite is thermodynamically stable within the boundaries shown.

Clearly, at the more negative values of G_{298}^O (pentlandite) chosen, the domain of stability of pentlandite is excessive, resulting in the disappearance of the single sulphide species regions and even some of the oxide, hydroxide, ionic species and pure-metal areas. This is incompatible with experience and common-sense.

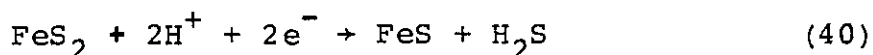
A sensible region of stability of pentlandite occurs when the G_{298}^O value lies in the range -179.66 (non-appearance) to -200 kcal mole⁻¹.

For a value of $G_{298}^O((\text{Fe,Ni})_9\text{S}_8) = -190$ kcal mole⁻¹, the stability region occurs entirely within the stable domain of the iron and nickel sulphides, and has a comparable extent of stability. As pentlandite occurs in nature in combination with iron and nickel sulphides, it might be reasonable to choose this value of G_{298}^O as being representative of the most likely (Fe-Ni-S-H₂O) system.

A complete diagram for the Fe-Ni-S-H₂O system, including pentlandite (where $G_{298}^O = -190$ kcal mole⁻¹), is given as an example in Diagram A3.8.

From Diagram A3.7, it can be seen that the region of stability approaches a limit as the G_{298}^O (pentlandite) value is made less negative. The limit occurs when the upper and lower boundaries of the stable region merge (and hence disappear) at the boundary between FeS and FeS₂, in an envelope of stable Ni₃S₂. This occurs in the presence of H₂S(aq), HS⁻(aq) and S²⁻(aq), dependent on pH.

Consider the boundary between FeS and FeS₂ (in the stable region of H₂S(aq)):

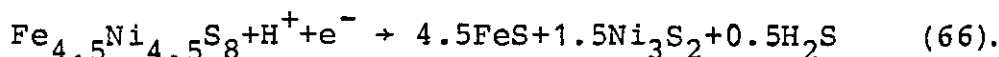
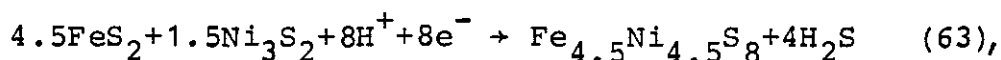


The Nernst Equation which defines this boundary is given by (40):

$$E_T = -0.1708 - 0.05916\text{pH} \quad (40),$$

at the assumed activities.

Similarly, for the boundaries between pentlandite and FeS_2 or FeS :



The corresponding Nernst Equations are:

$$E_T = - \frac{\Delta G_{298}^{\circ} \times 4184}{8 \times 96487} - 0.02958 \log\{\text{H}_2\text{S}\} - 0.05916\text{pH} \quad (63),$$

$$E_T = - \frac{\Delta G_{298}^{\circ} \times 4184}{96487} - 0.02958 \log\{\text{H}_2\text{S}\} - 0.05916\text{pH} \quad (66).$$

In all three cases, the "-0.05916pH" factor merely determines the slope of the boundary; the position is fixed by the terms involving ΔG_{298}° and $\log\{\text{H}_2\text{S}\}$.

For equations (40) and (63) to coincide:

$$-0.1708 = - \frac{\Delta G_{298}^{\circ} (\text{reaction 63}) \times 4184}{8 \times 96487} - 0.02958 \log(0.1),$$

$$\therefore \Delta G_{298}^{\circ} (\text{reaction 63}) = 36.968 \text{ kcal mole}^{-1},$$

$$\therefore G_{298}^{\circ} (\text{pentlandite}) = -186.59 \text{ kcal mole}^{-1}$$

(from data, Appendix A3.A1).

Check: for equations (40) and (66) to coincide:

$$-0.1708 = - \frac{\Delta G_{298}^{\circ} (\text{reaction 66}) \times 4184}{96487} - 0.02958 \log(0.1),$$

$$\therefore \Delta G_{298}^{\circ} (\text{reaction 66}) = 4.621 \text{ kcal mole}^{-1}$$

$$\therefore G_{298}^{\circ} (\text{pentlandite}) = -186.60 \text{ kcal mole}^{-1}$$

(from data, Appendix A3.A1).

Similarly for the boundaries in the presence of $\text{HS}^{-}(\text{aq})$ and $\text{S}^{2-}(\text{aq})$.

Thus, pentlandite will only appear on the E_{H} -pH diagram, under the conditions assumed, if $G_{298}^{\circ}(\text{pentlandite}) < -186.60 \text{ kcal mole}^{-1}$.

From above, the most likely value of $G_{298}^{\circ}(\text{Fe,Ni})_9\text{S}_8$ is approximately $-190 \text{ kcal mole}^{-1}$.

A3.4. Discussion

The diagrams produced show the thermodynamic stability regions of the species in aqueous solution, at 25°C , for the system $(\text{Fe-Ni-S-H}_2\text{O})$, including the mixed sulphide pentlandite.

The component diagrams are similar to those of the same system in reference (63), but extra species were considered in the $(\text{Ni-S-H}_2\text{O})$ system.

The diagrams are limited by the following considerations:

- species which appear are only those which are included in the calculations,
- they are dependent on the available thermodynamic data. In general, these were of established

accuracy, but the predicted value of pentlandite highlighted a problem. The data available were generally for the purest form of a compound, etc., of exact composition; no account could be taken of any non-stoichiometry,

- they represent thermodynamic stability regions only and no account is taken of kinetics,
- during calculation, water was assumed to be stable over the whole range; however, water has a region of stability and any region beyond this domain must be considered to be metastable (shown dotted on diagrams),
- calculations were based on activities rather than concentrations, but there is no reliable method available for determining activity coefficients,
- the diagrams are limited to the temperature, pressure and activities assumed for construction,
- the data were for pure substances only. In practice, even small amounts of other elements (notably alkali metals, Na and K) cause the formation of jarosites at low pH, in the presence of sulphate, so some care has to be exercised when considering a real, multi-element system (especially a mineral) in conjunction with a simplified Pourbaix Diagram.

The estimated value of $G_{298}^{\circ}(\text{pentlandite}) = -179.66 \text{ kcal mole}^{-1}$ seemed to be inconsistent with its expected stability. From consideration of the diagrams produced, a more realistic value might be $\sim -190 \text{ kcal mole}^{-1}$. However, theoretical evaluation does give a comparable result, in view of the possible errors in the predictive methods (outlined previously).

A3.5. Suggestions for further work

(i) The system could be considered at other activities, to give information which is more readily comparable with, for example, an industrial leaching process.

(ii) The system could be considered at elevated temperature to investigate the change in stability of the various species with temperature. Methods for extrapolation are thoroughly dealt with in references (59) and (71), which rely heavily on reference (70) for predictive methods of data extrapolation.

(iii) Since pentlandite typically has a range of composition, $(\text{Fe,Ni})_9\text{S}_8$ with $\text{Fe:Ni} = 0.8 \rightarrow 1.2$, an investigation might be undertaken to see how the stability of pentlandite varies with composition (chemical half-cells and, hence, line positions on the diagrams will change).

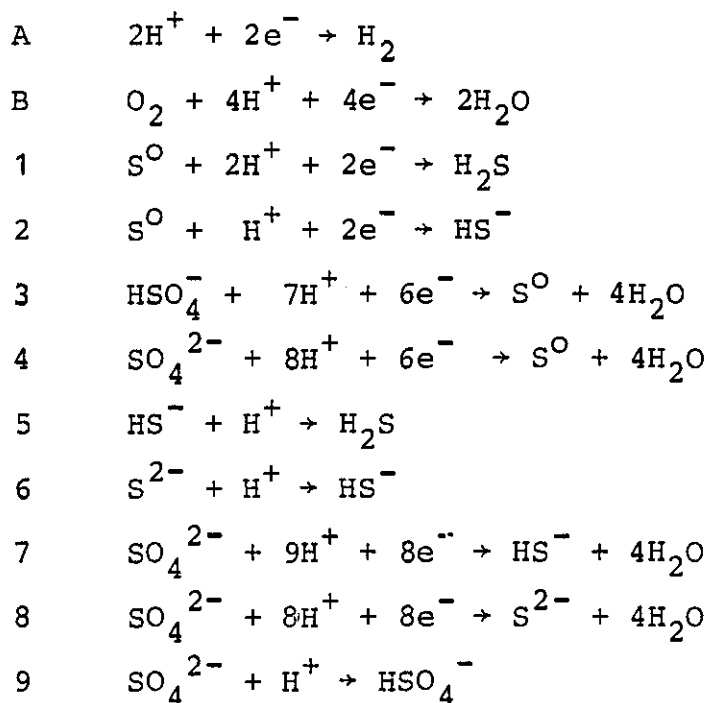
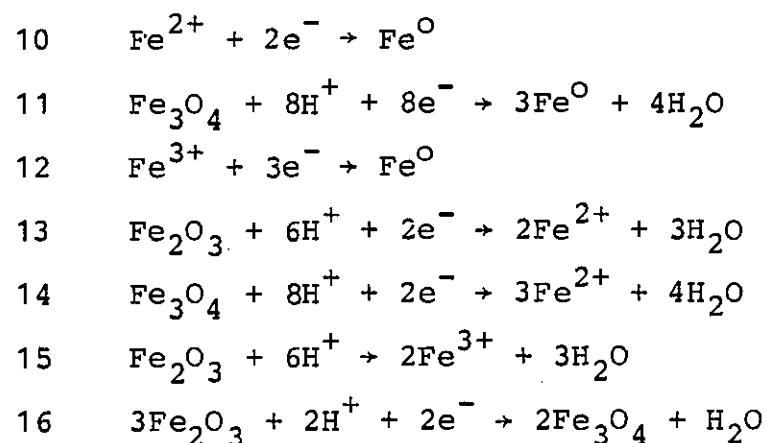
Appendix A3.A1

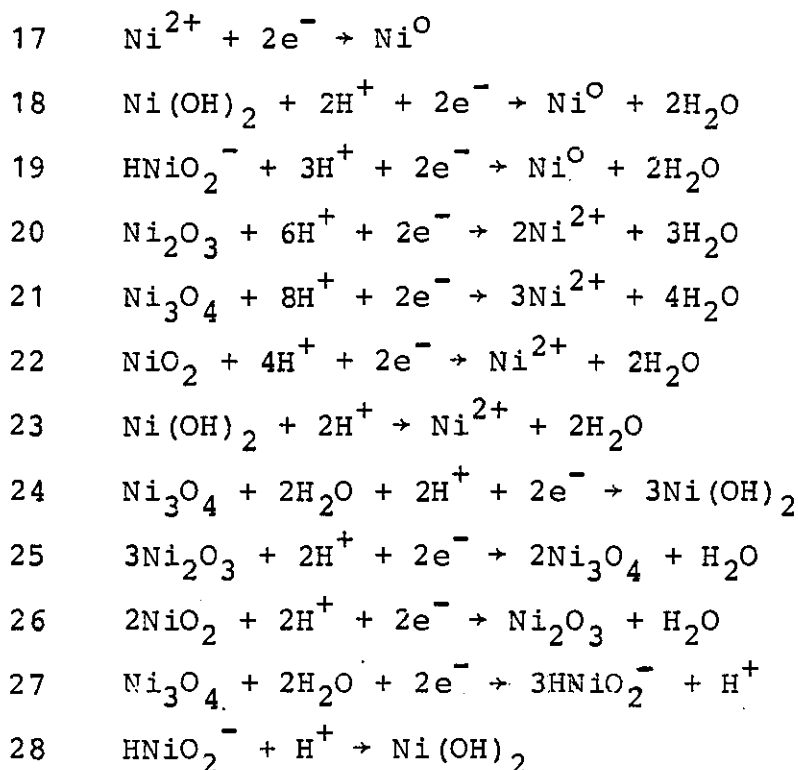
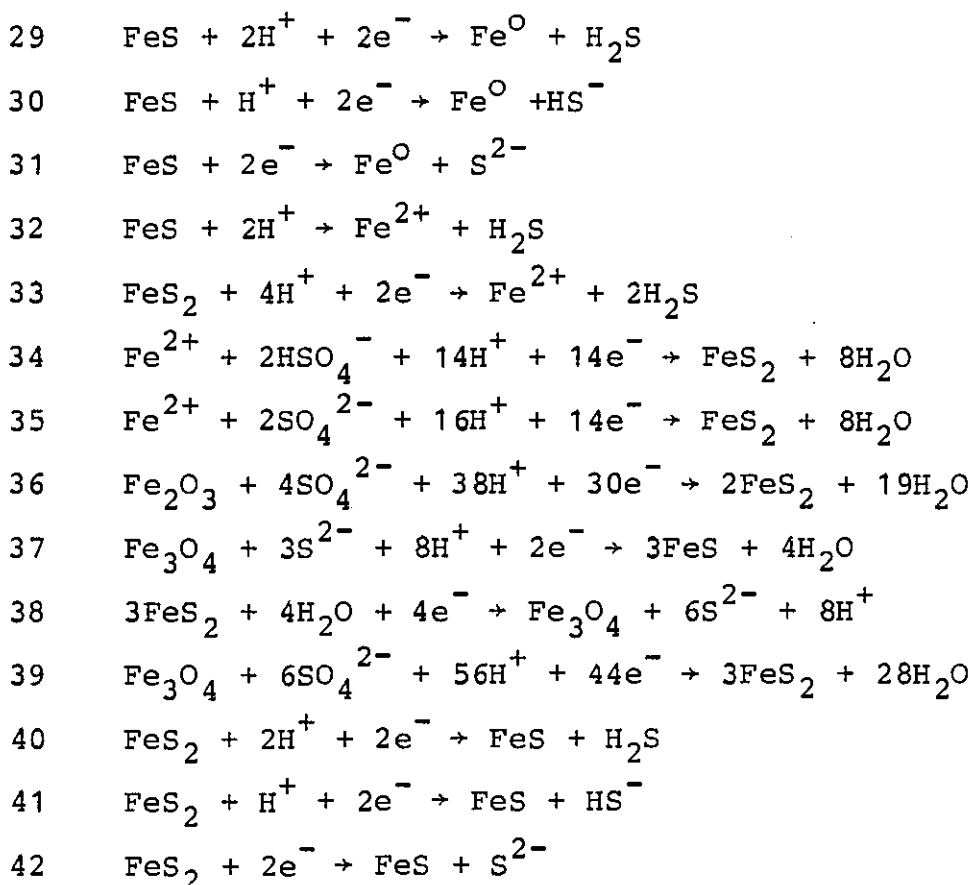
Species	G_{298}° kcal mole ⁻¹	Reference	Species	G_{298}° kcal mole ⁻¹	Reference
H ₂ O	-56.687	(61)	Ni ₃ O ₄	-170.15	(62)
H ₂	0	(60)	Ni ₂ O ₃	-112.27	(62)
O ₂	0	(60)	NiO ₂	-47.5	(63)
H ⁺ _(aq)	0	(60)	Ni(OH) ₂	-108.3	(63)
			HNiO ₂ ⁻ _(aq)	-83.46	(63)
Fe ⁰	0	(60)	NiS	-19.0	(61)
Fe ²⁺ _(aq)	-18.85	(61)	Ni ₃ S ₂	-47.1	(61)
Fe ³⁺ _(aq)	-1.1	(61)			
Fe ₂ O ₃	-177.4	(60)	S ⁰	0	(60)
Fe ₃ O ₄	-242.7	(60)	H ₂ S _(aq)	-6.66	(61)
FeS _α	-24.0	(60)	HS ⁻ _(aq)	2.88	(61)
FeS ₂	-39.9	(60)	S ²⁻ _(aq)	20.5	(61)
			HSO ₄ ⁻ _(aq)	-180.69	(61)
Ni ⁰	0	(60)	SO ₄ ²⁻ _(aq)	-177.97	(61)
Ni ²⁺ _(aq)	-10.9	(61)			
NiO	-50.6	(61)	(Fe,Ni) ₉ S ₈ pentlan- dite	-179.66	(64)

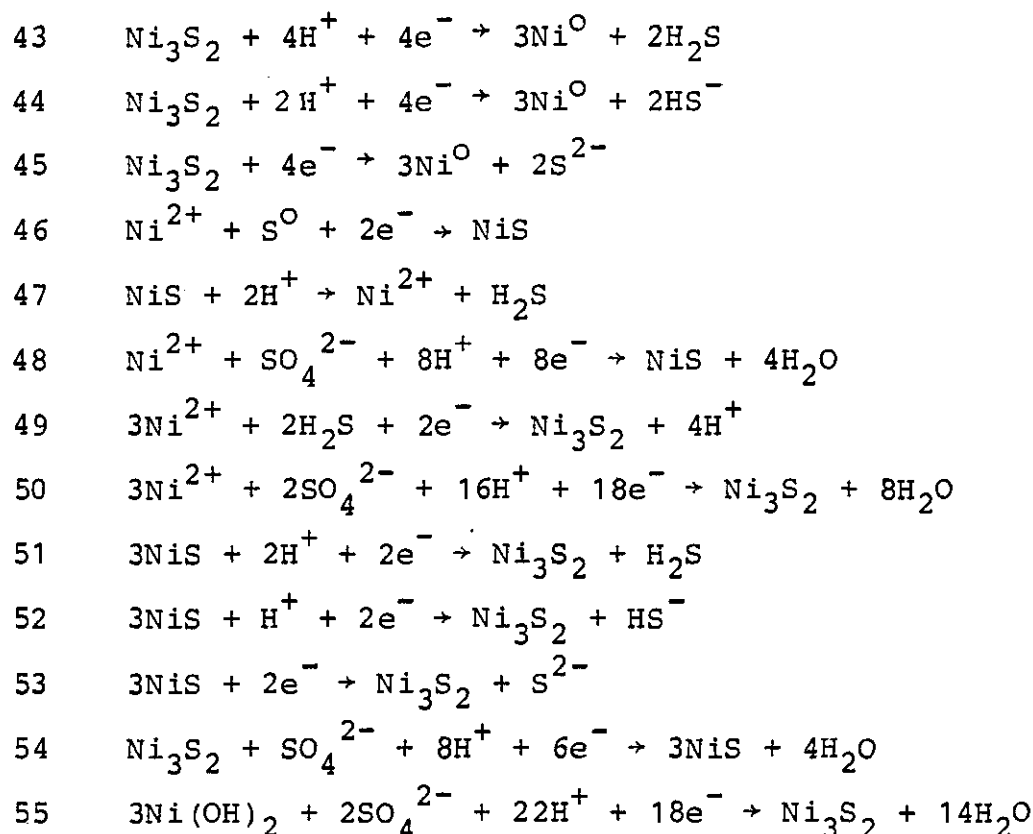
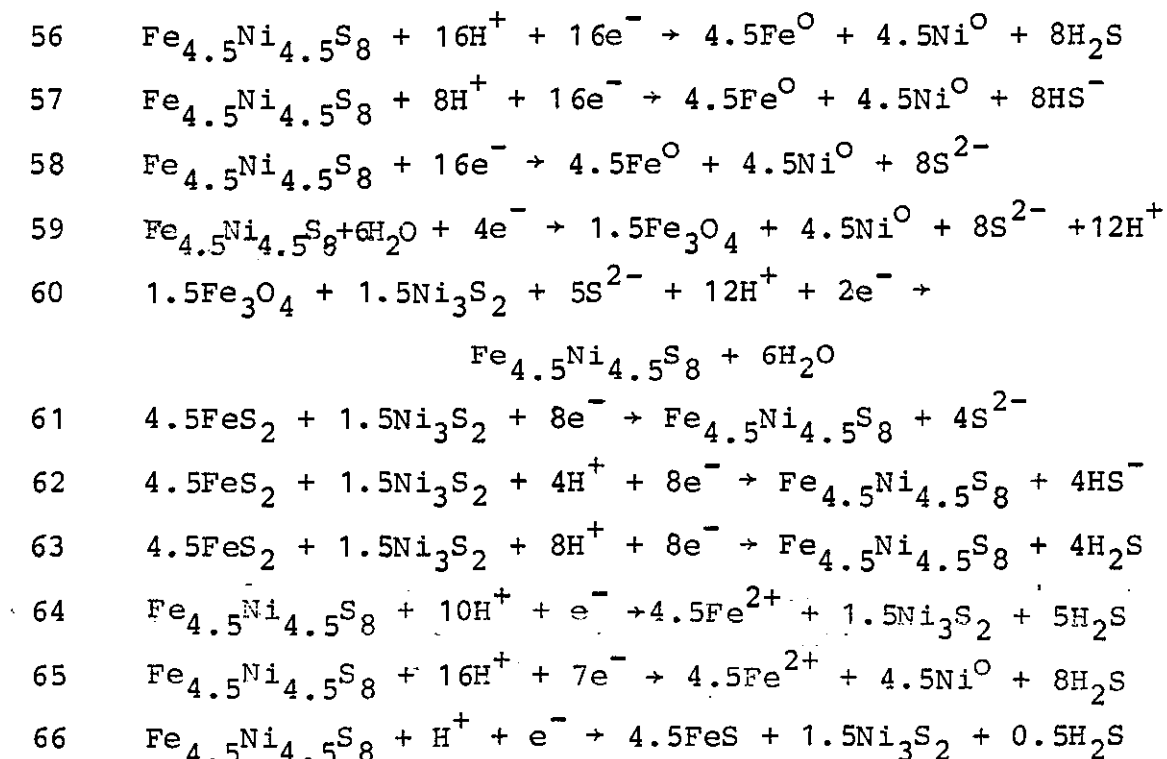
Table A3.1. Data used in calculations.

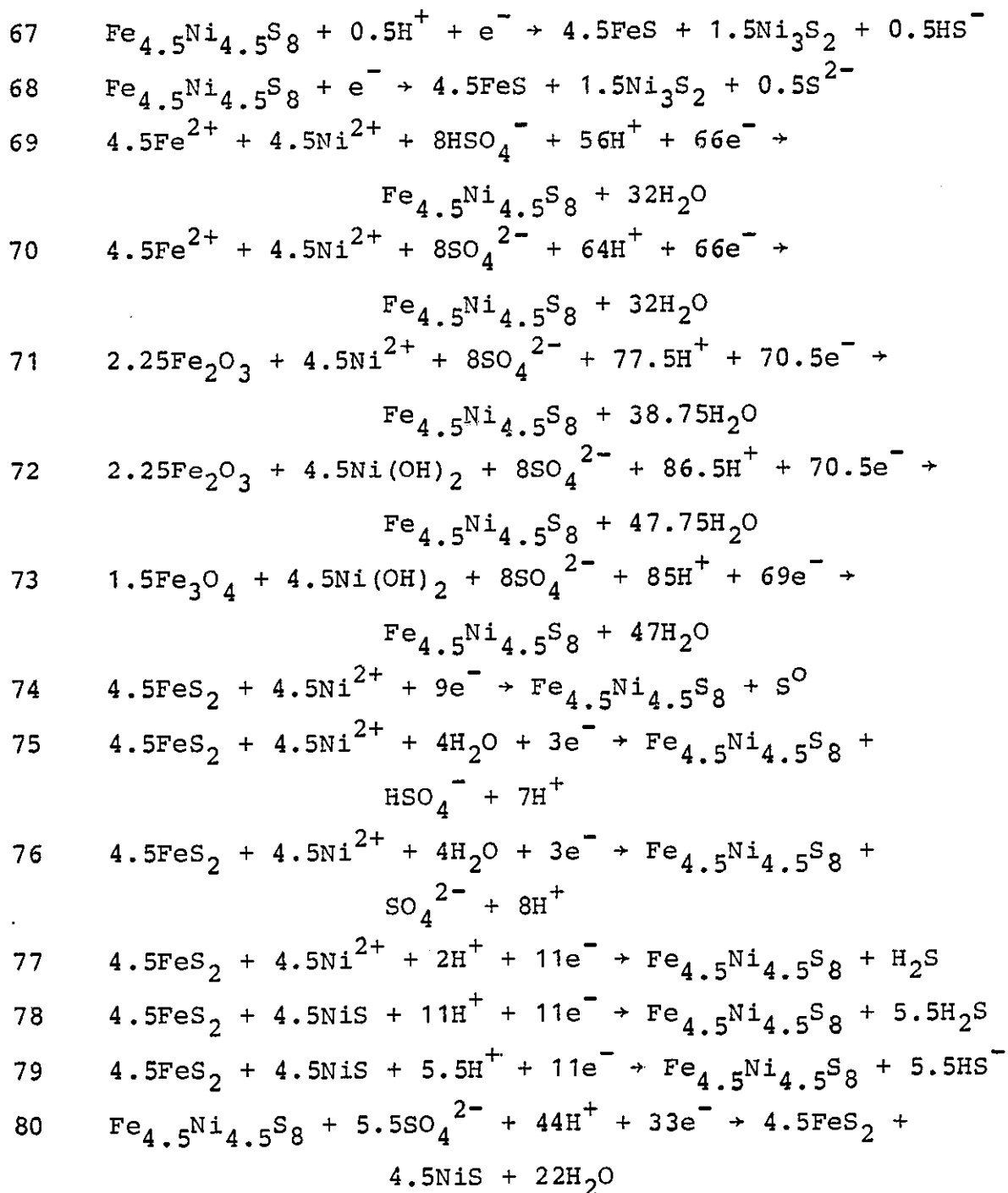
Appendix A3.A2

Chemical equations used in drawing diagrams - written
as half-cell reactions

A3.A2(i) S-H₂O speciesA3.A2(ii) Fe-H₂O species

A3.A2(iii) Ni-H₂O speciesA3.A2(iv) Fe-S-H₂O species

A3.A2(v) Ni-S-H₂O speciesA3.A2(vi) Fe-Ni-S-H₂O species



Appendix A3.A3

Numerical equations used in drawing diagrams - written
in terms of pH and activity of species

A3.A3 (i) S-H₂O species

- A $E_T = -0.0296 \log\{H_2\} - 0.05916 \text{pH}$
 B $E_T = 1.2291 + 0.0148 \log\{O_2\} - 0.05916 \text{pH}$
 1 $E_T = 0.1444 - 0.0296 \log\{H_2S\} - 0.05916 \text{pH}$
 2 $E_T = -0.0624 - 0.0296 \log\{HS^-\} - 0.0296 \text{pH}$
 3 $E_T = 0.3329 + 0.0099 \log\{HSO_4^-\} - 0.0690 \text{pH}$
 4 $E_T = 0.3525 + 0.0099 \log\{SO_4^{2-}\} - 0.0789 \text{pH}$
 5 $\text{pH} = 6.9930 - \log\{H_2S\} + \log\{HS^-\}$
 6 $\text{pH} = 12.9157 - \log\{HS^-\} + \log\{S^{2-}\}$
 7 $E_T = 0.2488 - 0.0074 \log\{HS^-\} + 0.0074 \log\{SO_4^{2-}\} - 0.0666 \text{pH}$
 8 $E_T = 0.1533 - 0.0074 \log\{S^{2-}\} + 0.0074 \log\{SO_4^{2-}\} - 0.05916 \text{pH}$
 9 $\text{pH} = 1.9938 - \log\{HSO_4^-\} + \log\{SO_4^{2-}\}$

A3.A3 (ii) Fe-H₂O species

- 10 $E_T = -0.4087 + 0.0296 \log\{Fe^{2+}\}$
 11 $E_T = -0.0865 - 0.05916 \text{pH}$
 12 $E_T = 0.7697 + 0.05916 \log\{Fe^{3+}\} - 0.05916 \log\{Fe^{2+}\}$
 13 $E_T = 0.6583 - 0.05916 \log\{Fe^{2+}\} - 0.1775 \text{pH}$
 14 $E_T = 0.8802 - 0.0887 \log\{Fe^{2+}\} - 0.2366 \text{pH}$
 15 $\text{pH} = -0.6278 - 0.3333 \log\{Fe^{3+}\}$
 16 $E_T = 0.2144 - 0.05916 \text{pH}$

A3.A3 (iii) Ni-H₂O species

- 17 $E_T = -0.2363 + 0.0296 \log\{Ni^{2+}\}$
 18 $E_T = 0.1100 - 0.05916 \text{pH}$
 19 $E_T = 0.6486 + 0.0296 \log\{HNiO_2^-\} - 0.0887 \text{pH}$
 20 $E_T = 1.7257 - 0.05916 \log\{Ni^{2+}\} - 0.1775 \text{pH}$
 21 $E_T = 1.9361 - 0.0887 \log\{Ni^{2+}\} - 0.2366 \text{pH}$
 22 $E_T = 1.6646 - 0.0296 \log\{Ni^{2+}\} - 0.1183 \text{pH}$
 23 $\text{pH} = 5.8546 - 0.5 \log\{Ni^{2+}\}$
 24 $E_T = 0.8971 - 0.05916 \text{pH}$

- 25 $E_T = 1.3047 - 0.05916\text{pH}$
 26 $E_T = 1.6035 - 0.05916\text{pH}$
 27 $E_T = -0.0002 - 0.0887\log\{\text{H}\text{NiO}_2^-\} + 0.0296\text{pH}$
 28 $\text{pH} = 18.2081 + \log\{\text{H}\text{NiO}_2^-\}$

A3.A3 (iv) Fe-S-H₂O species

- 29 $E_T = -0.3760 - 0.0296\log\{\text{H}_2\text{S}\} - 0.05916\text{pH}$
 30 $E_T = -0.5828 - 0.0296\log\{\text{HS}^-\} - 0.0296\text{pH}$
 31 $E_T = -0.9648 - 0.0296\log\{\text{S}^{2-}\}$
 32 $\text{pH} = 0.5535 - 0.5\log\{\text{H}_2\text{S}\} - 0.5\log\{\text{Fe}^{2+}\}$
 33 $E_T = -0.1676 - 0.0296\log\{\text{Fe}^{2+}\} - 0.05916\log\{\text{H}_2\text{S}\} - 0.1183\text{pH}$
 34 $E_T = 0.3505 + 0.0042\log\{\text{Fe}^{2+}\} + 0.0085\log\{\text{HSO}_4^-\} - 0.05916\text{pH}$
 35 $E_T = 0.3674 + 0.0042\log\{\text{Fe}^{2+}\} + 0.0085\log\{\text{SO}_4^{2-}\} - 0.0676\text{pH}$
 36 $E_T = 0.3868 + 0.0079\log\{\text{SO}_4^{2-}\} - 0.0749\text{pH}$
 37 $E_T = 2.5486 + 0.0887\log\{\text{S}^{2-}\} - 0.2366\text{pH}$
 38 $E_T = -2.4581 - 0.0887\log\{\text{S}^{2-}\} + 0.1183\text{pH}$
 39 $E_T = 0.3907 + 0.0081\log\{\text{SO}_4^{2-}\} - 0.0753\text{pH}$
 40 $E_T = -0.2003 - 0.0296\log\{\text{H}_2\text{S}\} - 0.05916\text{pH}$
 41 $E_T = -0.4072 - 0.0296\log\{\text{HS}^-\} - 0.0296\text{pH}$
 42 $E_T = -0.7892 - 0.0296\log\{\text{S}^{2-}\}$

A3.A3 (v) Ni-S-H₂O species

- 43 $E_T = -0.3662 - 0.0296\log\{\text{H}_2\text{S}\} - 0.05916\text{pH}$
 44 $E_T = -0.5730 - 0.0296\log\{\text{HS}^-\} - 0.0296\text{pH}$
 45 $E_T = -0.9551 - 0.0296\log\{\text{S}^{2-}\}$
 46 $E_T = 0.1756 + 0.0296\log\{\text{Ni}^{2+}\}$
 47 $\text{pH} = -0.5278 - 0.5\log\{\text{Ni}^{2+}\} - 0.5\log\{\text{H}_2\text{S}\}$
 48 $E_T = 0.3083 + 0.0074\log\{\text{Ni}^{2+}\} + 0.0074\log\{\text{SO}_4^{2-}\} - 0.05916\text{pH}$
 49 $E_T = 0.0234 + 0.0887\log\{\text{Ni}^{2+}\} + 0.05916\log\{\text{H}_2\text{S}\} + 0.1183\text{pH}$
 50 $E_T = 0.2697 + 0.0099\log\{\text{Ni}^{2+}\} + 0.0066\log\{\text{SO}_4^{2-}\} - 0.0526\text{pH}$
 51 $E_T = -0.0702 - 0.0296\log\{\text{H}_2\text{S}\} - 0.05916\text{pH}$
 52 $E_T = 0.2771 - 0.0296\log\{\text{HS}^-\} - 0.0296\text{pH}$
 53 $E_T = -0.6571 - 0.0296\log\{\text{S}^{2-}\}$
 54 $E_T = 0.4241 + 0.0099\log\{\text{SO}_4^{2-}\} - 0.0789\text{pH}$
 55 $E_T = 0.3852 + 0.0066\log\{\text{SO}_4^{2-}\} - 0.0723\text{pH}$

A3.A3 (vi) Fe-Ni-S-H₂O species

$$(a) \quad \underline{G_{298}^O \text{ (Pentlandite)} = -300 \text{ kcal mole}^{-1}}$$

- 56 $E_T = -0.6687 - 0.0296 \log\{H_2S\} - 0.05916pH$
 57 $E_T = -0.8755 - 0.0296 \log\{HS^-\} - 0.0296pH$
 58 $E_T = -1.2575 - 0.0296 \log\{S^{2-}\}$
 69 $E_T = 0.3512 + 0.0040 \log\{Fe^{2+}\} + 0.0040 \log\{Ni^{2+}\}$
 $\quad + 0.0072 \log\{HSO_4^-\} - 0.0502pH$
 70 $E_T = 0.3655 + 0.0040 \log\{Fe^{2+}\} + 0.0040 \log\{Ni^{2+}\}$
 $\quad + 0.0072 \log\{SO_4^{2-}\} - 0.0574pH$
 71 $E_T = 0.3842 + 0.0038 \log\{Ni^{2+}\} + 0.0067 \log\{SO_4^{2-}\} - 0.0650pH$
 72 $E_T = 0.4284 + 0.0067 \log\{SO_4^{2-}\} - 0.0726pH$
 73 $E_T = 0.4331 + 0.0069 \log\{SO_4^{2-}\} - 0.0729pH$

Other lines not applicable.

$$(b) \quad \underline{G_{298}^O \text{ (Pentlandite)} = -275 \text{ kcal mole}^{-1}}$$

- 56 $E_T = -0.6009 - 0.0296 \log\{H_2S\} - 0.05916pH$
 57 $E_T = -0.8078 - 0.0296 \log\{HS^-\} - 0.0296pH$
 58 $E_T = -1.1898 - 0.0296 \log\{S^{2-}\}$
 74 $E_T = 0.2236 + 0.0296 \log\{Ni^{2+}\}$
 75 $E_T = 0.0049 + 0.0887 \log\{Ni^{2+}\} - 0.0197 \log\{HSO_4^-\} + 0.1380pH$
 76 $E_T = -0.0344 + 0.0887 \log\{Ni^{2+}\} - 0.0197 \log\{SO_4^{2-}\} + 0.1578pH$
 70 $E_T = 0.3491 + 0.0040 \log\{Fe^{2+}\} + 0.0040 \log\{Ni^{2+}\}$
 $\quad + 0.0072 \log\{SO_4^{2-}\} - 0.0574pH$
 71 $E_T = 0.3688 + 0.0038 \log\{Ni^{2+}\} + 0.0067 \log\{SO_4^{2-}\} - 0.0650pH$
 72 $E_T = 0.4131 + 0.0067 \log\{SO_4^{2-}\} - 0.0726pH$
 73 $E_T = 0.4174 + 0.0069 \log\{SO_4^{2-}\} - 0.0729pH$

Other lines not applicable

$$(c) \quad \underline{G_{298}^O \text{ (Pentlandite)} = -250 \text{ kcal mole}^{-1}}$$

- 56 $E_T = -0.5332 - 0.0296 \log\{H_2S\} - 0.05916pH$
 57 $E_T = -0.7400 - 0.0296 \log\{HS^-\} - 0.0296pH$
 58 $E_T = -1.1220 - 0.0296 \log\{S^{2-}\}$

77	$E_T = 0.1106 + 0.0242 \log\{\text{Ni}^{2+}\} - 0.0054 \log\{\text{H}_2\text{S}\} - 0.0108 \text{pH}$
78	$E_T = 0.0851 - 0.0296 \log\{\text{H}_2\text{S}\} - 0.0591 \text{pH}$
79	$E_T = -0.1218 - 0.0296 \log\{\text{HS}^-\} - 0.0296 \text{pH}$
80	$E_T = 0.3723 + 0.0099 \log\{\text{SO}_4^{2-}\} - 0.0789 \text{pH}$
76	$E_T = -0.3957 + 0.0887 \log\{\text{Ni}^{2+}\} - 0.0197 \log\{\text{SO}_4^{2-}\} + 0.1578 \text{pH}$
71	$E_T = 0.3535 + 0.0038 \log\{\text{Ni}^{2+}\} + 0.0067 \log\{\text{SO}_4^{2-}\} - 0.0650 \text{pH}$
72	$E_T = 0.3977 + 0.0067 \log\{\text{SO}_4^{2-}\} - 0.0726 \text{pH}$
73	$E_T = 0.4017 + 0.0069 \log\{\text{SO}_4^{2-}\} - 0.0729 \text{pH}$

Other lines not applicable

(d) $\underline{G_{298}^{\text{O}}(\text{Pentlandite}) = -225 \text{ kcal mole}^{-1}}$

56	$E_T = -0.4654 - 0.0296 \log\{\text{H}_2\text{S}\} - 0.0591 \text{pH}$
57	$E_T = -0.6722 - 0.0296 \log\{\text{HS}^-\} - 0.0296 \text{pH}$
58	$E_T = -1.0543 - 0.0296 \log\{\text{S}^{2-}\}$
59	$E_T = -3.9577 - 0.1183 \log\{\text{S}^{2-}\} + 0.1775 \text{pH}$
77	$E_T = 0.0121 + 0.0242 \log\{\text{Ni}^{2+}\} - 0.0054 \log\{\text{H}_2\text{S}\} - 0.0108 \text{pH}$
78	$E_T = -0.0135 - 0.0296 \log\{\text{H}_2\text{S}\} - 0.0591 \text{pH}$
79	$E_T = -0.2203 - 0.0296 \log\{\text{HS}^-\} - 0.0296 \text{pH}$
80	$E_T = 0.4052 + 0.0099 \log\{\text{SO}_4^{2-}\} - 0.0789 \text{pH}$
71	$E_T = 0.3381 + 0.0038 \log\{\text{Ni}^{2+}\} + 0.0067 \log\{\text{SO}_4^{2-}\} - 0.0650 \text{pH}$
72	$E_T = 0.3805 + 0.0068 \log\{\text{SO}_4^{2-}\} - 0.0728 \text{pH}$
73	$E_T = 0.3865 + 0.0070 \log\{\text{SO}_4^{2-}\} - 0.0732 \text{pH}$

Other lines not applicable

(e) $\underline{G_{298}^{\text{O}}(\text{Pentlandite}) = -200 \text{ kcal mole}^{-1}}$

56	$E_T = -0.3976 - 0.0296 \log\{\text{H}_2\text{S}\} - 0.0591 \text{pH}$
57	$E_T = -0.6045 - 0.0296 \log\{\text{HS}^-\} - 0.0296 \text{pH}$
58	$E_T = -0.9865 - 0.0296 \log\{\text{S}^{2-}\}$
59	$E_T = -3.6867 - 0.1183 \log\{\text{S}^{2-}\} + 0.1775 \text{pH}$
60	$E_T = 4.5081 + 0.1479 \log\{\text{S}^{2-}\} - 0.3550 \text{pH}$
61	$E_T = -0.7166 - 0.0296 \log\{\text{S}^{2-}\}$
62	$E_T = -0.3345 - 0.0296 \log\{\text{HS}^-\} - 0.0296 \text{pH}$

- 63 $E_T = -0.1277 - 0.0296 \log\{H_2S\} - 0.05916pH$
 64 $E_T = -0.4868 - 0.2662 \log\{Fe^{2+}\} - 0.2958 \log\{H_2S\} - 0.5916pH$
 65 $E_T = -0.3834 - 0.0670 \log\{H_2S\} - 0.038 \log\{Fe^{2+}\} - 0.1352pH$

Other lines not applicable

(f) $\underline{G_{298}^O(\text{Pentlandite}) = -190 \text{ kcal mole}^{-1}}$

- 66 $E_T = -0.3478 - 0.0296 \log\{H_2S\} - 0.05916pH$
 67 $E_T = -0.5546 - 0.0296 \log\{HS^-\} - 0.0296pH$
 68 $E_T = -0.9366 - 0.0296 \log\{S^{2-}\}$
 60 $E_T = 4.2913 + 0.1479 \log\{S^{2-}\} - 0.3550pH$
 61 $E_T = -0.7708 - 0.0296 \log\{S^{2-}\}$
 62 $E_T = -0.3888 - 0.0296 \log\{HS^-\} - 0.0296pH$
 63 $E_T = -0.1819 - 0.0296 \log\{H_2S\} - 0.05916pH$
 64 $E_T = -0.0531 - 0.2662 \log\{Fe^{2+}\} - 0.2958 \log\{H_2S\} - 0.5916pH$

Other lines not applicable

(g) $\underline{G_{298}^O(\text{Pentlandite}) = -188 \text{ kcal mole}^{-1}}$

- 66 $E_T = -0.2610 - 0.0296 \log\{H_2S\} - 0.05916pH$
 67 $E_T = -0.4679 - 0.0296 \log\{HS^-\} - 0.0296pH$
 68 $E_T = -0.8499 - 0.0296 \log\{S^{2-}\}$
 60 $E_T = 4.2479 + 0.1479 \log\{S^{2-}\} - 0.3550pH$
 61 $E_T = -0.7816 - 0.0296 \log\{S^{2-}\}$
 62 $E_T = -0.3996 - 0.0296 \log\{HS^-\} - 0.0296pH$
 63 $E_T = -0.1928 - 0.0296 \log\{H_2S\} - 0.05916pH$
 64 $E_T = 0.0336 - 0.2662 \log\{Fe^{2+}\} - 0.2958 \log\{H_2S\} - 0.5916pH$

Other lines not applicable

APPENDIX A3.A4

Numerical equations used in drawing diagrams - written
in terms of pH at chosen activities

A3.A4(i) S-H₂O species

A	$E_T = -0.05916\text{pH}$
B	$E_T = 1.2291 - 0.05916\text{pH}$
1	$E_T = 0.1740 - 0.05916\text{pH}$
2	$E_T = -0.0329 - 0.0296\text{pH}$
3	$E_T = 0.3230 - 0.0690\text{pH}$
4	$E_T = 0.3427 - 0.0789\text{pH}$
5	$\text{pH} = 6.9930$
6	$\text{pH} = 12.9157$
7	$E_T = 0.2488 - 0.0666\text{pH}$
8	$E_T = 0.1533 - 0.05916\text{pH}$
9	$\text{pH} = 1.9938$

A3.A4(ii) Fe-H₂O species

10	$E_T = -0.4383\text{V}$
11	$E_T = -0.0865 - 0.05916\text{pH}$
12	$E_T = 0.7697\text{V}$
13	$E_T = 0.7174 - 0.1775\text{pH}$
14	$E_T = 0.9690 - 0.2366\text{pH}$
15	$\text{pH} = -0.2945$
16	$E_T = 0.2144 - 0.05916\text{pH}$

A3.A4(iii) Ni-H₂O species

17	$E_T = -0.2659\text{V}$
18	$E_T = 0.1100 - 0.05916\text{pH}$
19	$E_T = 0.6190 - 0.0887\text{pH}$
20	$E_T = 1.7848 - 0.1775\text{pH}$
21	$E_T = 2.0249 - 0.2366\text{pH}$
22	$E_T = 1.6942 - 0.1183\text{pH}$
23	$\text{pH} = 6.3546$

24	$E_T = 0.8971 - 0.05916\text{pH}$
25	$E_T = 1.3047 - 0.05916\text{pH}$
26	$E_T = 1.6035 - 0.05916\text{pH}$
27	$E_T = 0.0885 + 0.0296\text{pH}$
28	$\text{pH} = 17.2081$

A3.A4 (iv) Fe-S-H₂O species

29	$E_T = -0.3464 - 0.05916\text{pH}$
30	$E_T = -0.5532 - 0.0296\text{pH}$
31	$E_T = -0.9353\text{V}$
32	$\text{pH} = 1.5534$
33	$E_T = -0.0789 - 0.1183\text{pH}$
34	$E_T = 0.3378 - 0.05916\text{pH}$
35	$E_T = 0.3547 - 0.0676\text{pH}$
36	$E_T = 0.3789 - 0.0749\text{pH}$
37	$E_T = 2.4599 - 0.2366\text{pH}$
38	$E_T = -2.3694 + 0.1183\text{pH}$
39	$E_T = 0.3826 - 0.0753\text{pH}$
40	$E_T = -0.1708 - 0.05916\text{pH}$
41	$E_T = -0.3776 - 0.0296\text{pH}$
42	$E_T = -0.7596\text{V}$

A3.A4 (v) Ni-S-H₂O species

43	$E_T = -0.3366 - 0.05916\text{pH}$
44	$E_T = -0.5435 - 0.0296\text{pH}$
45	$E_T = -0.9255\text{V}$
46	$E_T = 0.1460\text{V}$
47	$\text{pH} = 0.4722$
48	$E_T = 0.2935 - 0.05916\text{pH}$
49	$E_T = -0.1245 + 0.1183\text{pH}$
50	$E_T = 0.2533 - 0.0526\text{pH}$
51	$E_T = -0.0407 - 0.05916\text{pH}$
52	$E_T = -0.2475 - 0.0296\text{pH}$
53	$E_T = -0.6295\text{V}$
54	$E_T = 0.4142 - 0.0789\text{pH}$
55	$E_T = 0.3786 - 0.0723\text{pH}$

A3.A4(vi) Fe-Ni-S-H₂O species

$$(a) \quad \underline{G_{298}^O(\text{Pentlandite})} = -300 \text{ kcal mole}^{-1}$$

56	$E_T = -0.6391-0.05916\text{pH}$
57	$E_T = -0.8459-0.0296\text{pH}$
58	$E_T = -1.2280\text{V}$
69	$E_T = 0.3360-0.0502\text{pH}$
70	$E_T = 0.3503-0.0574\text{pH}$
71	$E_T = 0.3737-0.0650\text{pH}$
72	$E_T = 0.4217-0.0726\text{pH}$
73	$E_T = 0.4262-0.0729\text{pH}$

Other lines not applicable

$$(b) \quad \underline{G_{298}^O(\text{Pentlandite})} = -275 \text{ kcal mole}^{-1}$$

56	$E_T = -0.5713-0.05916\text{pH}$
57	$E_T = -0.7782-0.0296\text{pH}$
58	$E_T = -1.1602\text{V}$
74	$E_T = 0.1940\text{V}$
75	$E_T = -0.0641-0.1380\text{pH}$
76	$E_T = -0.1034+0.1578\text{pH}$
70	$E_T = 0.3339-0.0574\text{pH}$
71	$E_T = 0.3584-0.0650\text{pH}$
72	$E_T = 0.4063-0.0726\text{pH}$
73	$E_T = 0.4105-0.0729\text{pH}$

Other lines not applicable

$$(c) \quad \underline{G_{298}^O(\text{Pentlandite})} = -250 \text{ kcal mole}^{-1}$$

56	$E_T = -0.5036-0.05916\text{pH}$
57	$E_T = -0.7104-0.0296\text{pH}$
58	$E_T = -1.0924\text{V}$
77	$E_T = 0.0918-0.0108\text{pH}$
78	$E_T = 0.1147-0.05916\text{pH}$
79	$E_T = -0.0922-0.0296\text{pH}$
80	$E_T = 0.3624-0.0789\text{pH}$

76	$E_T = -0.4648 + 0.1578\text{pH}$
71	$E_T = 0.3430 - 0.0650\text{pH}$
72	$E_T = 0.3910 - 0.0726\text{pH}$
73	$E_T = 0.3948 - 0.0729\text{pH}$

Other lines not applicable

$$(d) \underline{G_{298}^O(\text{Pentlandite}) = -225 \text{ kcal mole}^{-1}}$$

56	$E_T = -0.4358 - 0.05916\text{pH}$
57	$E_T = -0.6427 - 0.0296\text{pH}$
58	$E_T = -1.0247\text{V}$
59	$E_T = -3.8394 + 0.1775\text{pH}$
77	$E_T = -0.0068 - 0.0108\text{pH}$
78	$E_T = 0.0161 - 0.05916\text{pH}$
79	$E_T = -0.1907 - 0.0296\text{pH}$
80	$E_T = 0.3953 - 0.0789\text{pH}$
71	$E_T = 0.3276 - 0.0650\text{pH}$
72	$E_T = 0.3737 - 0.0728\text{pH}$
73	$E_T = 0.3794 - 0.0732\text{pH}$

Other lines not applicable

$$(e) \underline{G_{298}^O(\text{Pentlandite}) = -200 \text{ kcal mole}^{-1}}$$

56	$E_T = -0.3681 - 0.05916\text{pH}$
57	$E_T = -0.5749 - 0.0296\text{pH}$
58	$E_T = -0.9569\text{V}$
59	$E_T = -3.5683 + 0.1775\text{pH}$
60	$E_T = 4.3602 - 0.3550\text{pH}$
61	$E_T = -0.6870\text{V}$
62	$E_T = -0.3050 - 0.0296\text{pH}$
63	$E_T = -0.0981 - 0.05916\text{pH}$
64	$E_T = 0.0753 - 0.5916\text{pH}$
65	$E_T = -0.2778 - 0.1352\text{pH}$

Other lines not applicable

$$(f) \quad \underline{G_{298}^O(\text{Pentlandite}) = -190 \text{ kcal mole}^{-1}}$$

66	$E_T = -0.3182-0.05916\text{pH}$
67	$E_T = -0.5250-0.0296\text{pH}$
68	$E_T = -0.9071\text{V}$
60	$E_T = 4.1434-0.3550\text{pH}$
61	$E_T = -0.7412\text{V}$
62	$E_T = -0.3592-0.0296\text{pH}$
63	$E_T = -0.1523-0.05916\text{pH}$
64	$E_T = 0.5089-0.5916\text{pH}$

Other lines not applicable

$$(g) \quad \underline{G_{298}^O(\text{Pentlandite}) = -188 \text{ kcal mole}^{-1}}$$

66	$E_T = -0.2315-0.05916\text{pH}$
67	$E_T = -0.4383-0.0296\text{pH}$
68	$E_T = -0.8203\text{V}$
60	$E_T = 4.1000-0.3550\text{pH}$
61	$E_T = -0.7520\text{V}$
62	$E_T = -0.3700-0.0296\text{pH}$
63	$E_T = -0.1632-0.05916\text{pH}$
64	$E_T = 0.5956-0.5916\text{pH}$

Other lines not applicable.

APPENDIX A3.A5List of diagrams

All diagrams drawn for 25°C; activity of solid species = 1; activities of dissolved and ionic species = 0.1; a_{H_2} , a_{O_2} , a_{H_2O} = 1.

<u>Diagram</u>	<u>System</u>
A3.1	S-H ₂ O
A3.2	Fe-H ₂ O
A3.3	Ni-H ₂ O
A3.4	Fe-S-H ₂ O
A3.5	Ni-S-H ₂ O
A3.6	Fe-Ni-S-H ₂ O in the absence of a mixed sulphide
A3.7	Region of stability of pentlandite for varying G_{298}^O (Fe,Ni) ₉ S ₈ compatible with the stable species of diagram A3.6
A3.8	Fe-Ni-S-H ₂ O including pentlandite when G_{298}^O (Pentlandite) = -190 kcal mole ⁻¹ .

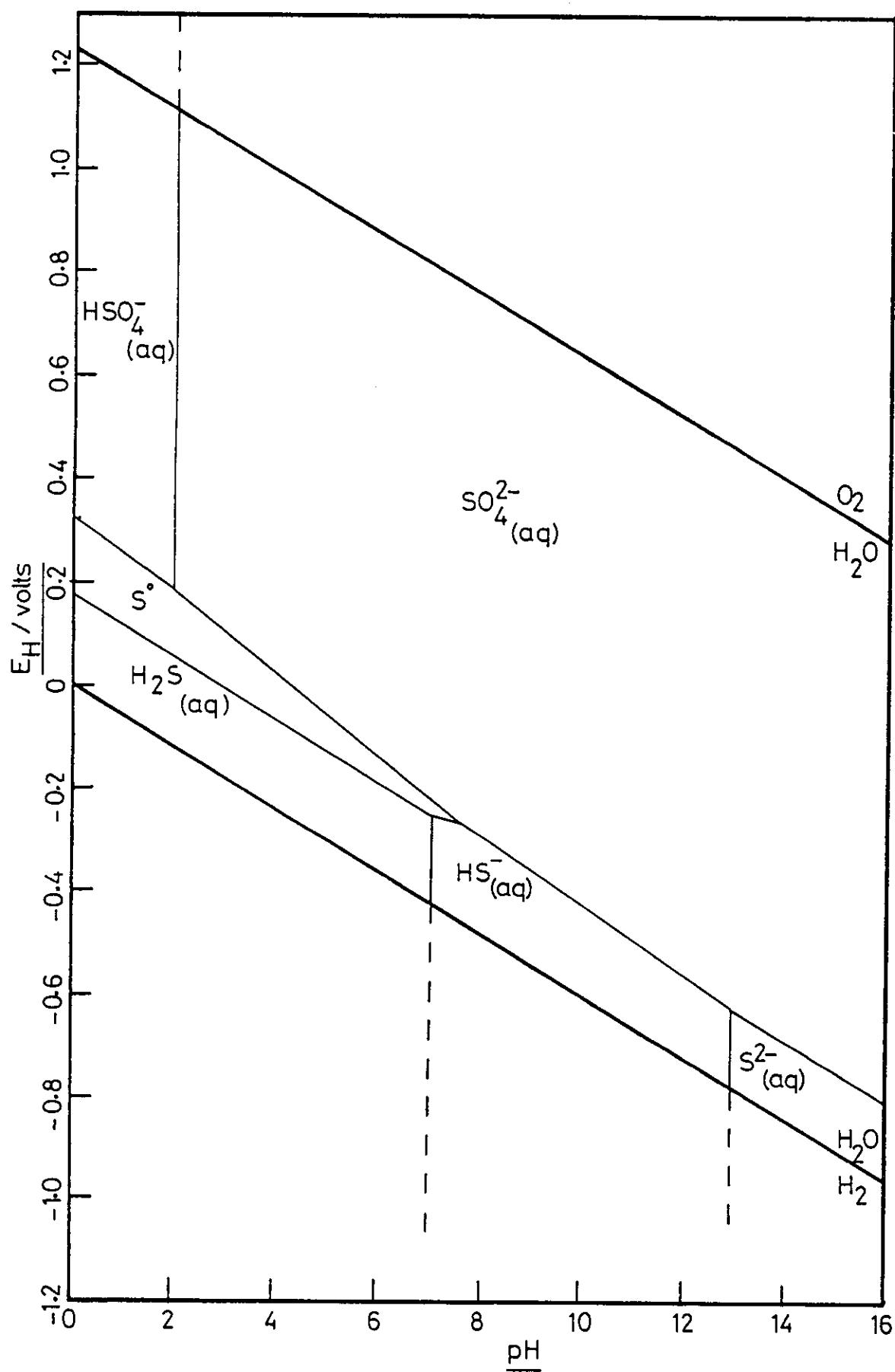


Diagram 1 S-H₂O

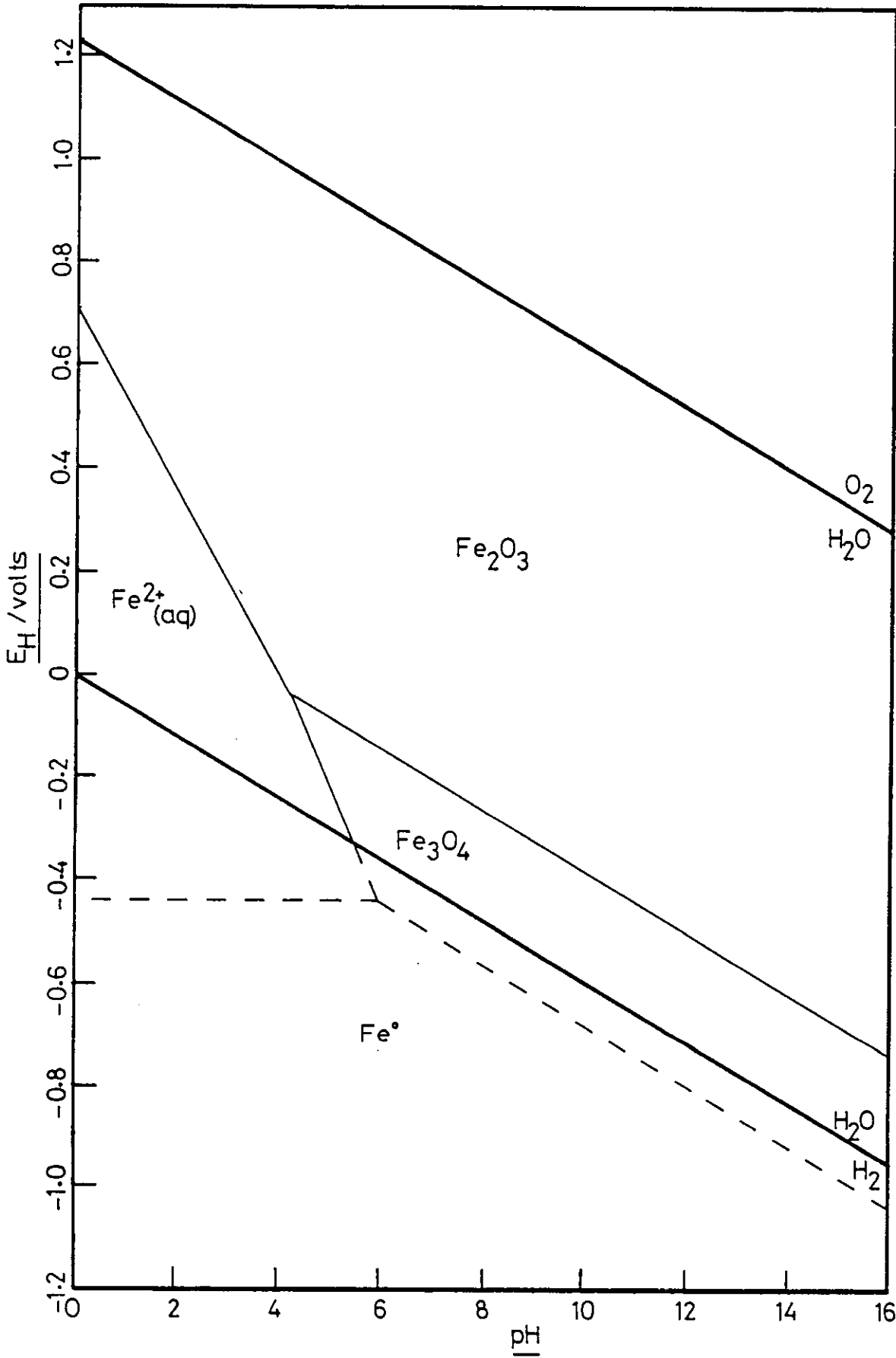


Diagram 2 Fe-H₂O

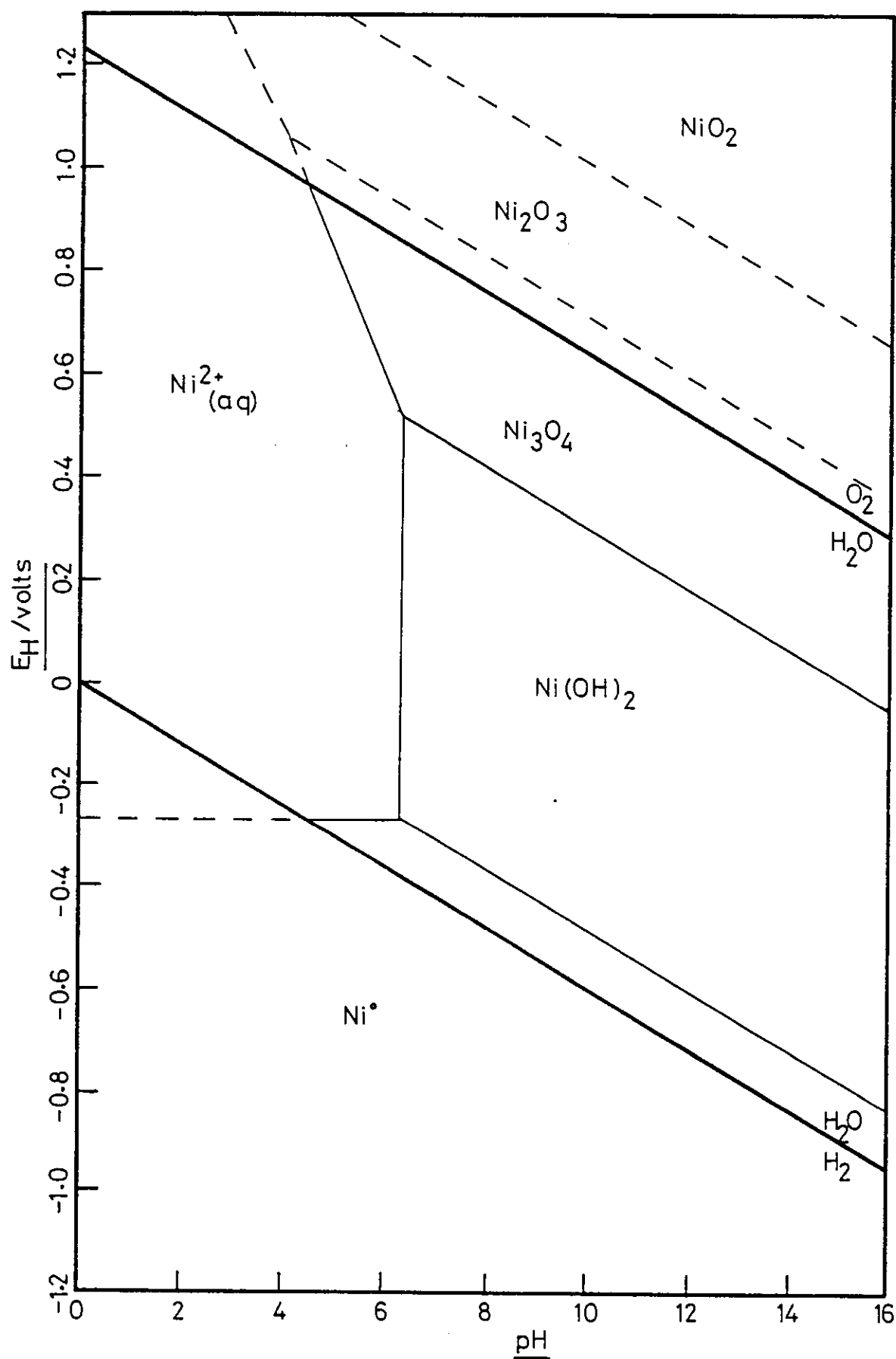


Diagram 3 Ni - H₂O

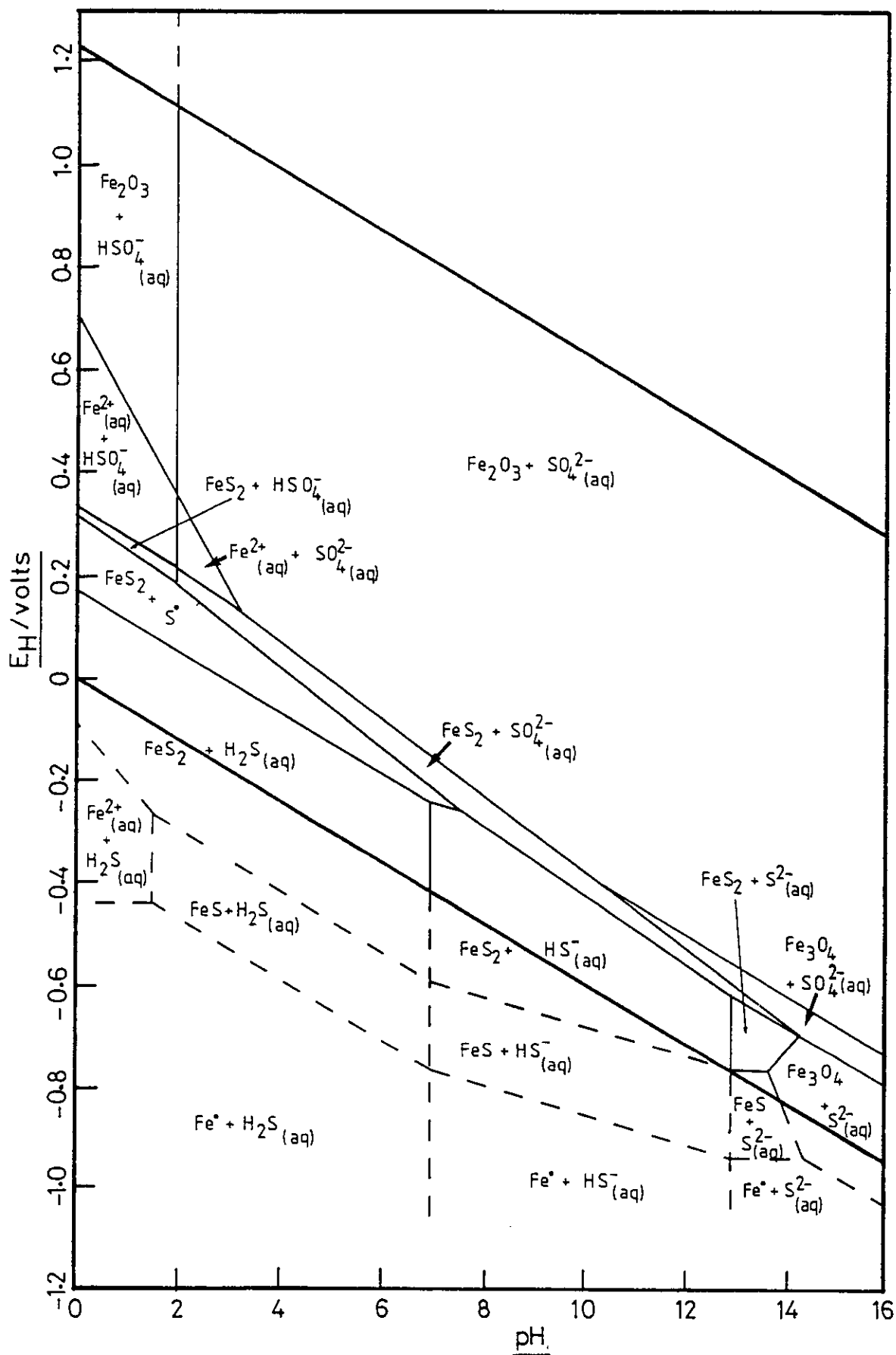


Diagram 4 Fe - S - H₂O

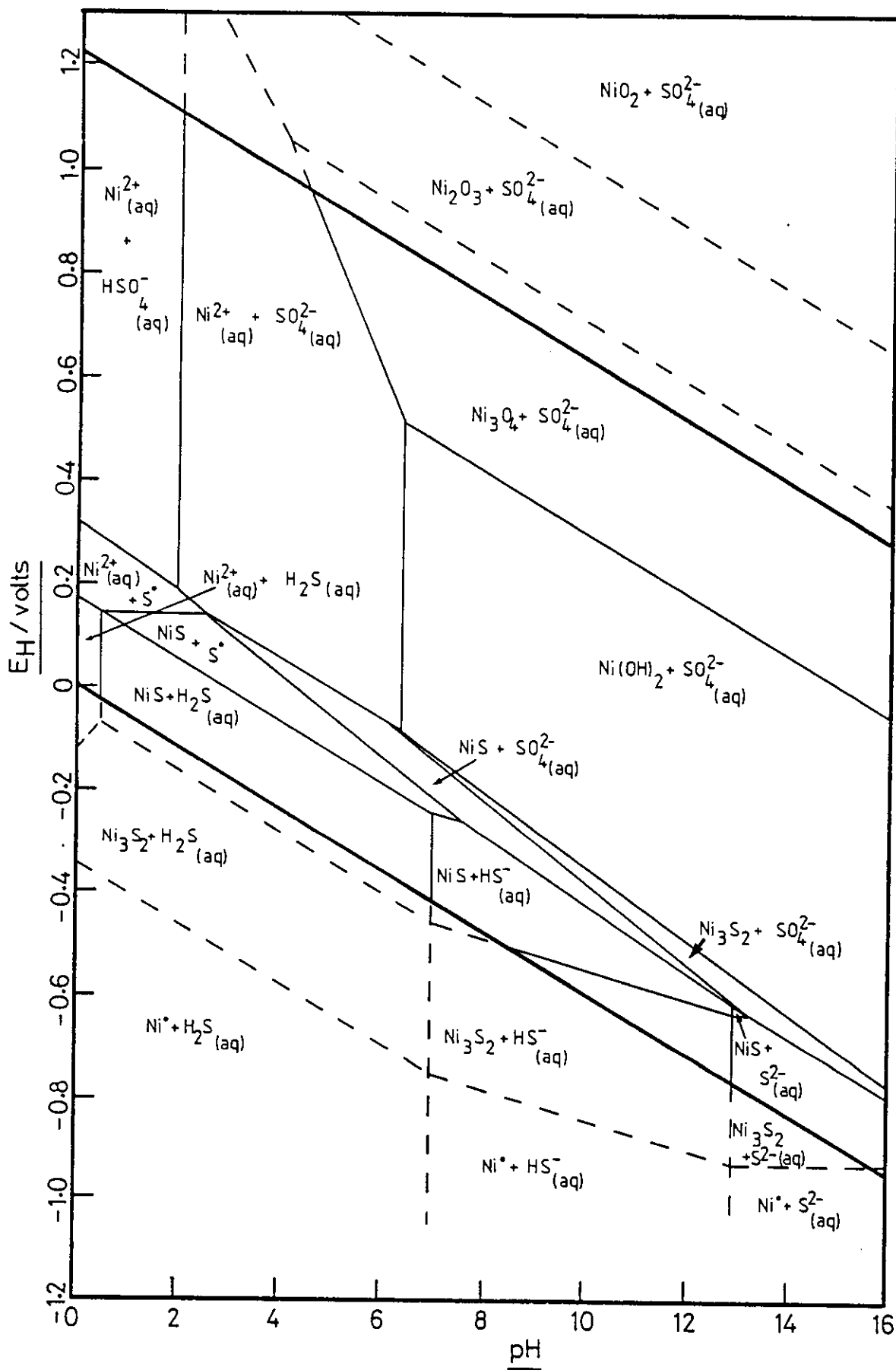


Diagram 5 Ni-S-H₂O

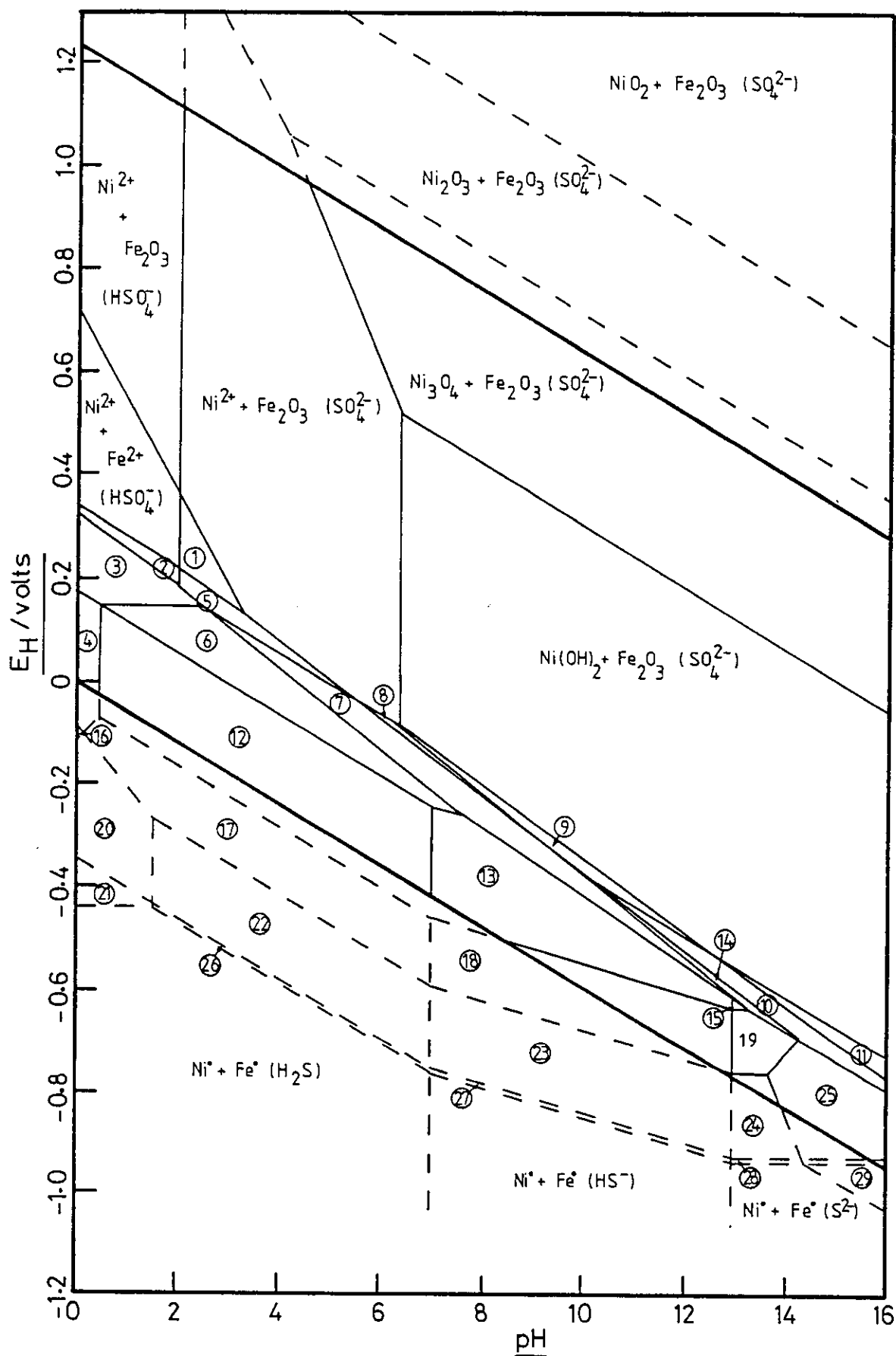


Diagram 6 Fe - Ni - S - H₂O (no mixed sulphide)

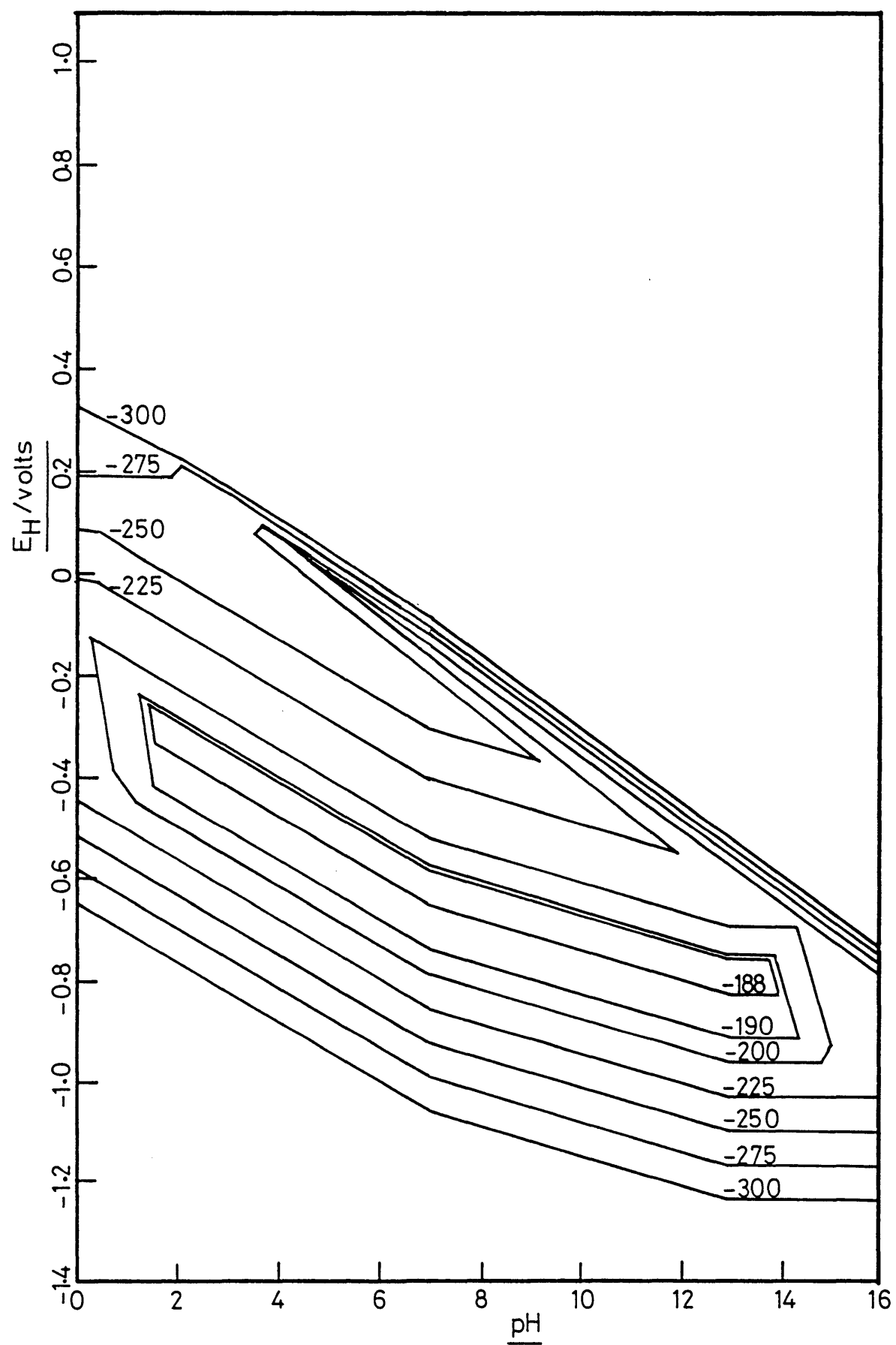


Diagram 7 Stability regions of $(\text{Fe,Ni})_9\text{S}_8$ consistent with
Diagram 6

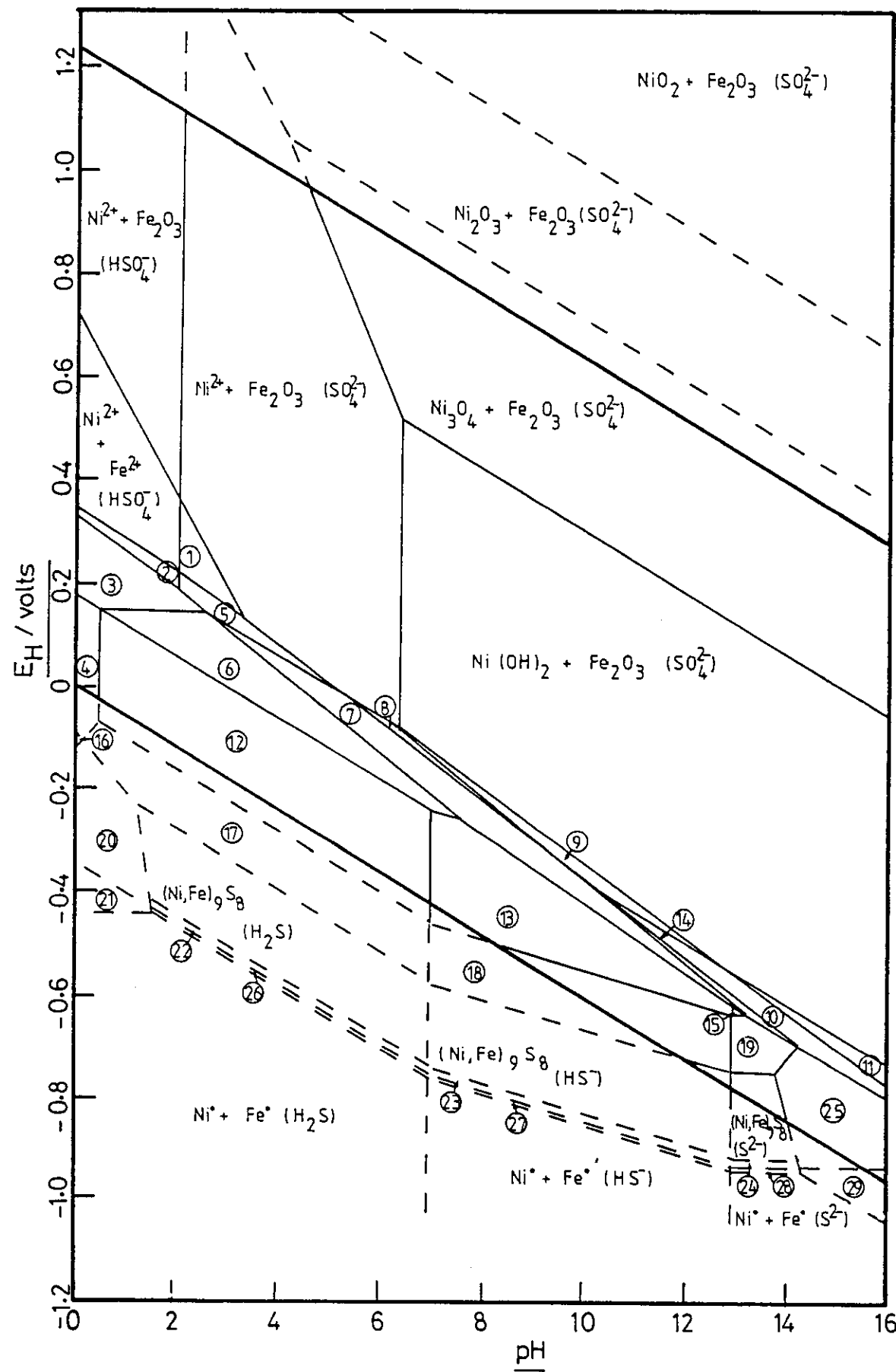


Diagram 8 Fe - Ni - S - H₂O [with (Fe,Ni)₉S₈]

APPENDIX A3.A6Key

Key to stable phases in diagrams A3.6 and A3.8

1	$\text{Ni}^{2+} + \text{Fe}^{2+} (\text{SO}_4^{2-})$	25	$\text{Ni}_3\text{S}_2 + \text{Fe}_3\text{O}_4 (\text{S}^{2-})$
2	$\text{Ni}^{2+} + \text{FeS}_2 (\text{HSO}_4^-)$	26	$\text{Ni}^0 + \text{FeS} (\text{H}_2\text{S})$
3	$\text{Ni}^{2+} + \text{FeS}_2 (\text{S}^0)$	27	$\text{Ni}^0 + \text{FeS} (\text{HS}^-)$
4	$\text{Ni}^{2+} + \text{FeS}_2 (\text{H}_2\text{S})$	28	$\text{Ni}^0 + \text{FeS} (\text{S}^{2-})$
5	$\text{Ni}^{2+} + \text{FeS}_2 (\text{SO}_4^{2-})$	29	$\text{Ni}^0 + \text{Fe}_3\text{O}_4 (\text{S}^{2-})$
6	$\text{NiS} + \text{FeS}_2 (\text{S}^0)$		
7	$\text{NiS} + \text{FeS}_2 (\text{SO}_4^{2-})$		
8	$\text{NiS} + \text{Fe}_2\text{O}_3 (\text{SO}_4^{2-})$		
9	$\text{Ni}_3\text{S}_2 + \text{Fe}_2\text{O}_3 (\text{SO}_4^{2-})$		
10	$\text{Ni}_3\text{S}_2 + \text{Fe}_3\text{O}_4 (\text{SO}_4^{2-})$		
11	$\text{Ni}(\text{OH})_2 + \text{Fe}_3\text{O}_4 (\text{SO}_4^{2-})$		
12	$\text{NiS} + \text{FeS}_2 (\text{H}_2\text{S})$		
13	$\text{NiS} + \text{FeS}_2 (\text{HS}^-)$		
14	$\text{Ni}_3\text{S}_2 + \text{FeS}_2 (\text{SO}_4^{2-})$		
15	$\text{NiS} + \text{FeS}_2 (\text{S}^{2-})$		
16	$\text{Ni}^{2+} + \text{Fe}^{2+} (\text{H}_2\text{S})$		
17	$\text{Ni}_3\text{S}_2 + \text{FeS}_2 (\text{H}_2\text{S})$		
18	$\text{Ni}_3\text{S}_2 + \text{FeS}_2 (\text{HS}^-)$		
19	$\text{Ni}_3\text{S}_2 + \text{FeS}_2 (\text{S}^{2-})$		
20	$\text{Ni}_3\text{S}_2 + \text{Fe}^{2+} (\text{H}_2\text{S})$		
21	$\text{Ni}^0 + \text{Fe}^{2+} (\text{H}_2\text{S})$		
22	$\text{Ni}_3\text{S}_2 + \text{FeS} (\text{H}_2\text{S})$		
23	$\text{Ni}_3\text{S}_2 + \text{FeS} (\text{HS}^-)$		
24	$\text{Ni}_3\text{S}_2 + \text{FeS} (\text{S}^{2-})$		

ACKNOWLEDGEMENTS

The author wishes to express his special thanks to his supervisor, Professor A.R. Burkin, Professor of Hydrometallurgy, for his invaluable guidance and encouragement throughout the course of this project.

The author would like to extend his gratitude to members of the Hydrometallurgy Group, past and present, for their friendship and many fruitful discussions. Special mentions are due to Dr. Gary Manning for his advice, John Burgess for his technical expertise and Fiona Doyle for proof-reading this thesis.

In addition, the author wishes to express his appreciation to his many friends of the past three years, especially everyone associated with Keogh Hall, 1979-81. There was never a dull moment.

The author is grateful to Interlox Chemicals Ltd. for supplying the Rio Algom ore and undertaking X.R.F. analyses.

Thanks are extended to Sylvia Greenwood for her fast and immaculate typing of this thesis.

Acknowledgement is due to the Science Research Council for their financial support during the three years of research.

Finally, the author is greatly indebted to his parents and sister, without whose constant support and encouragement, none of this would have been possible.

W.M. Sajik
November, 1981.

REFERENCES

1. A.R. Burkin. "Extractive Metallurgy of Uranium", in Topics in Non-Ferrous Extractive Metallurgy, ed. A.R. Burkin, Critical Reports on Applied Chemistry, Volume 1, 1980. Blackwell Scientific Publications.
2. R.C. Merritt. The Extractive Metallurgy of Uranium, pub. Colorado School of Mines Research Institute - United States Atomic Energy Commission, 1971.
3. J.W. Clegg and D.D. Foley. Uranium Ore Processing, pub. Addison-Wesley, 1958. (Prepared under contract with the U.S.A.E.C.).
4. Minobras (E.A. Elevatorski - Manager). Uranium Ores and Minerals, pub. Minobras, 1977.
5. R.J. Trail. A preliminary account of the mineralogy of radioactive conglomerates in the Blind River region, Ontario. Can. Min. Journ. Vol. 75, 63-68, (1954).
6. F.L. Hess and R.C. Wells. Brannerite, a new uranium mineral, pub. Journal of the Franklin Institute, (1920). Vol. 89, Jan.-June, pp.225-237. (Also a note to this paper in the above publication, pp.779-80).
7. C. Palache, H. Berman and C. Frondel. The System of Mineralogy (of J.W. and E.S. Dana). Vol. 1, pub. J. Wiley and Sons, 1944.
8. N.P. Galkin, A.A. Maiorov and U.D. Veryatin. The Technology of the Treatment of Uranium Concentrates, pub. International Series of Monographs on Nuclear Energy, Vol. 1, pub. Pergamon Press, 1963, pp.20-21.
9. C.F. Davidson. On the occurrence of uranium in ancient conglomerates, pub. Economic Geology, v52, 1957, pp.668-91.
10. P. Ramdohr. Die "Pronto-Reaktion", pub, Neues Jahrbuch Für Mineralogie. Monatshefte (1957), 217.
11. P. Ramdohr. The Ore-Minerals and their Intergrowths, pub. Pergamon Press, 1969.
12. J.E. Patchett and E.W. Nuffield. Studies of radioactive compounds. X - The synthesis and crystallography of brannerite, pub. Can. Mineral, (1960), v.6, 483. (Also A.S.T.M. diffraction pattern 12-477).
13. S.W. Holmes. The Pronto Mine - Geology, pub. Western Miner and Oil Review, v.29, p.121, 1956.

14. B.G. Macdermid and L.G. Guglielmin. Uranium Milling at Stanrock Uranium Mines Ltd.. Some Economic Evaluations; in Unit Processes in Hydrometallurgy. M.E. Wandsworth and F.T. Davis, Eds. Metallurgical Society Conferences, vol. 24. Gordon and Breach Science Publishers, New York, 1964, pp.869-885.
15. A. Pabst. The metamict state, pub. American Mineralogist, vol. 37, 1952, pp.137-157.
16. D.R. George. Mineralogy of Uranium and Thorium-Bearing Minerals, pub. U.S.A.E.C., 1949, RMO-563.
17. D. Langmuir. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits, pub. Geochimica et Cosmochimica Acta, 1978, vol. 42, pp.547-569.
18. H.Y. Sohn and M.E. Wadsworth (eds.). Rate Processes of Extractive Metallurgy, pub. Plenum Press, 1979.
19. I.H. Warren and E.A. Devuyt. Leaching of metal oxides. In International Symposium on Hydrometallurgy, Chicago, Illinois, U.S.A., 1973, A.I.M.E.
20. E. Peters. The physical chemistry of hydrometallurgy. In International Symposium on Hydrometallurgy, Chicago, Illinois, U.S.A., 1973, A.I.M.E.
21. D.R. George. Recovery of Uranium from Climax Brannerite Concentrate C-7, pub, U.S.A.E.C. Report MITG-231, Massachusetts Institute of Technology, 1950.
22. K.D. Hester. Current developments at Rio Algom, Elliot Lake. Proceedings of the 8th Annual C.I.M. Hydrometallurgical Meeting, Montreal, August 1978.
23. E. LaRocque and E. Pakkala. Current leaching and product recovery practice at Denison Mines Limited. Proceedings of the 8th Annual C.I.M. Hydrometallurgical Meeting, Montreal, August 1978.
24. K.D. Hester. Rio Algom Ltd. Private communication, 1979.
25. Interlox Chemicals Ltd. Private communication, 1979.
26. M.J. Nicol, C.R.S. Needes and N.P. Finkelstein. Electrochemical model for the leaching of uranium dioxide:1 acid media. In Leaching and Reduction in Hydrometallurgy, A.R. Burkin, ed. London: Institution of Mining and Metallurgy, 1975, pp.1-11.
27. R.C. Weast (ed.). CRC Handbook of Chemistry and Physics. 60th edition, 1979-80. CRC Press.

28. G. Arthur and D. Scott. The effect of TiO_2 additions on the sintering of UO_2 . Trans. Brit. Ceram. Soc., vol. 63, 1964, pp.417-26.
29. J.B. Ainscough, F. Rigby and S.C. Osborn. J.Nucl. Mater., vol. 52, 1974, pp.191-203.
30. S.G. Tresvyatskii and V.I. Kushakovskii, Soviet J. At. Energy, vol. 8, 1961, pp.51-2.
31. L. Gmelin. Gmelin's Handbuch der anorganischen Chemie, 8 Auflage, 1975, Uran Ergänzungsband, Teil C3 Verbindungen, System Nr. 55.
32. J.R. Johnson and H.G. Sowman. In J. Belle, Uranium Dioxide, Properties and Nuclear Applications, Washington D.C., 1961.
33. J.F. Watson and D.R. Wilder. Iowa State Report No. 221, 1960; N.S.A. vol. 15, 1961, Nr. 31180.
34. H.G. Sowman and G.L. Ploetz. KAPL-1556, 1956, pp.1-27; N.S.A. vol. 11, 1957, Nr. 8754.
35. H.J. Matzke. AECL-2585, 1966, pp.1-34; N.S.A. vol. 20, 1966, Nr. 39381.
36. J.E. May and R.L. Stoute. AECL-2169, p.1149; N.S.A. vol. 19, 1965, Nr. 18448.
37. H. Landspersky and M. Voboril. J. Inorg. Nucl. Chem. vol. 29, 1967, pp.250-2.
38. V.S. Darshne and V.V. Deshpande. Proc. Chem. Symp. Bombay, India, 1972, book 2, pp.315-8; C.A. 81, 1974, 180427.
39. S.J. Kiss and M.M. Ristic. Sprechsaal, vol. 98, 1965, pp.859-62; C.A. 64, 1966, 13686.
40. Ö. Öztunali. Über die Struktur von Brannerit. pub. Neues Jahrbuch für Mineralogie, Monatshefte, 1959, pp.187-8.
41. H. Schröcke. Neues Jahrb. Mineral. Monatsh., 1958, pp.70-1.
42. M. Schidlowski. Neues Jahrb Mineral. Monatsh., Abhandl. 105, 1966, 310-24.
43. S. Kaiman. Synthesis of brannerite, pub. Can. Mineral, 1959, vol.6(3), pp.389-90.
44. J.C. Bobo. Rev. Chim. Minerale. vol. 1, 1964, pp.3-37.

45. H. Radzewitz. KFK-433, 1966, pp.1-53; N.S.A. vol. 21, 1967, Nr. 16652.
46. A. Pabst. Brannerite from California, pub. Am. Min., 1954, vol. 39, p.109. (Also A.S.T.M. diffraction pattern index, card 8-2).
47. P. Lussiez, K. Osseo-Asare and G. Simokovich. Effect of solid state impurities on the dissolution of nickel oxide. Metallurgy Department, The Pennsylvania State University, (unpublished).
48. Interlox Chemicals Ltd. Caro's acid laboratory procedure for hydrometallurgy (Widnes, Cheshire: The Company n.d.). Booklet A.0.5.2.
49. D.A. Johnson and T.M. Florence. Spectrophotometric determination of uranium (VI) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. Anal. Chim. Acta., vol. 53, 1971, p.73-9.
50. D.A. Johnson and T.M. Florence. A study of some pyridylazo dyestuffs as chromogenic reagents and the elucidation of the nature of their metal complex spectra. Talanta, vol. 22, 1975, pp.253-65.
51. Laporte Industries Limited. Private communication.
52. G.D. Manning. Imperial College. Private communication.
53. A.I. Vogel. A Textbook of Quantitative Inorganic Analysis. 3rd edition, 1961. Longmans.
54. Perkin Elmer Limited. Analytical Methods for Atomic Absorption Spectrophotometry, 1978.
55. J.H.E. Jeffes. Metallurgy Department, Imperial College, Undergraduate Course notes.
56. B. Terry. Ph.D. Thesis, University of London, 1981.
57. A.J. Monhemius. Precipitation diagrams for metal hydroxides, sulphides, arsenates and phosphates. Trans. Inst. Mining. Metallurgy, 1977, Vol.86, C202-6.
58. Dictionary of Geological Terms. Prepared under the direction of the American Geological Institute. Revised addition 1976.

The following references are relevant to Appendix 3.

59. P.J. Wyborn. Ph.D. Thesis, University of London, 1980.
60. O. Kubaschewski and C.B. Alcock. Metallurgical Thermochemistry, Pergamon, 5th edition, 1979.
61. D.D. Wagman, et al. N.B.S. Technical Note 270-3,4,5,6, N.B.S., U.S. Department of Commerce, 1969.
62. M. Pourbaix. Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, Cebelcor, 1966.
63. R.M. Garrels and C.L. Christ. Solutions, Minerals and Equilibria, Harper and Row, 1965.
64. T.I. Barry. National Physical Laboratories, Teddington, Middlesex. Private Communication, 1980.
65. D.R. Stull et al. J.A.N.A.F. Thermochemical Tables.
66. K.C. Mills. Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides, Butterworths, 1971.
67. W.E. Latimer. Oxidation Potentials, Prentice Hall, New Jersey, 2nd edition, 1952.
68. Barin and Knacke. Thermochemical Properties of Inorganic Substances, Supplement, 1977.
69. H.E. Barner and R.V. Scheuerman. Handbook of Thermochemical Data for Compounds and Aqueous Species, Wiley-Interscience, 1978.
70. C.M. Criss and J.W. Cobble. J. Am. Chem. Soc. vol. 86, 5385, 1964.
71. R.C.H. Ferreira. from Leaching and Reduction in Hydrometallurgy (ed. A.R. Burkin), I.M.M., 1975.
72. B.R. Conrad, R. Sridhar and J.S. Warner. High Temperature Enthalpies of Nickel Sulphides. Paper presented at the 100th Annual A.I.M.E. Meeting, Atlanta, Georgia, 1977.