

THE SOLVENT EXTRACTION OF AQUEOUS BORON SPECIES FROM
SOLUTIONS AND SLURRIES WITH 2-ETHYL-1,3-HEXANEDIOL AND
2-CHLORO-4-(1,1,3,3-TETRAMETHYL-BUTYL)-6-METHYLOL-PHENOL

A thesis submitted for the degree of
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"TO MY DEAREST WIFE"

ABSTRACT

The work herein represents a study of the boron industry, boron minerals and one aspect of laboratory processing: the solvent extraction of borates.

A review is given of the reserves, technology, uses, marketing, prices, recent developments and industrial prospects relevant to boron minerals, with particular reference to the Turkish industry. The main theme for laboratory study emerging from the review - control of borate pollution from effluent slurries at production plants - is introduced.

The collection of ore samples and slurries from location in Turkey and their detailed sampling, sample preparation and appraisal are described. Similarly, methods of synthesis and assay are given: the organic extractant 2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylol-phenol (CTMP) is synthesised from commercially available reagents and assayed by a newly developed spectrophotometric method; and borates are assayed by modified acid/base and colorimetric methods.

The design and operation are detailed of a mixer-settler and a sieve-plate pulse column for carrying out laboratory solvent extraction experiments with petroleum spirit solutions of CTMP and 2-ethyl-1,3-hexanediol (EHD). Comparison in operation with conventional shake-flask equipment is made.

The shake-flask technique has been used in conjunction with the diol solutions mentioned to determine the extraction characteristics of aqueous borates in the presence (variously) of the ions Na^+ , Ca^{2+} , Mg^{2+}

and Cl^- , all of which were found to be transferred in part across the interface dependent upon the contact time, pH, and concentrations of reagents. Equilibrium, % extraction against pH, and continuous variation curves indicated the existence of a synergistic effect between CTMP and EHD which appeared to involve a 1:1:1 ratio of the solvent and borate species.

Experiments employing optimized pulse column conditions in open-circuit have been carried out to assess the possibilities of extracting borates from both synthetic and industrial samples of aqueous slurry by solvent-in-pulp operation. The main solids considered are bentonite, quartz and calcite. Over 90% extraction was found to occur in a single stage without serious difficulties with phase separation, under these conditions at pH 9.2, 5% solids and 500 ppm B using 0.5 M 1:1 CTMP/EHD. Several successive extractions in partial closed-circuit could be used to reduce boron levels in the aqueous phase to less than 5 ppm while leaving over 99 - 99.9% of the solids unaffected. Calcite interacts strongly with the solvent but does not result in the serious formation of crud at the interface.

A preliminary industrial flowsheet has been developed on the basis of above-mentioned experimental work suitably upscaled. This is discussed in terms of selective removal of boron from alkaline plant-end slurries in Turkey, and also in terms of the solvent losses estimated to be incurred by dissolution, adsorption and entrainment in the aqueous phase.

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CONTENTS

	page
ABSTRACT	i
ACKNOWLEDGEMENTS	iii
LIST OF CONTENTS	iv
CHAPTER 1 INTRODUCTION	1
1.1 The borate industry	2
1.1.1 Reserves of borates	3
1.1.2 Technology	8
1.1.3 Uses	12
1.1.4 Marketing	15
1.1.5 Prices	17
1.1.6 Future of the borate industry	18
1.2 Turkish boron industry	18
1.2.1 Geology and formation of the deposits	20
1.2.2 Turkish mine sites	22
1.2.3 Markets and future outlook	27
1.3 Recent developments	28
1.4. Aims of the present work	36
CHAPTER 2 SAMPLING AND MINERAL APPRAISAL	38
2.1 Boron minerals	38
2.2 Sampling and assay	47
2.2.1 Head sampling	47
2.2.2 Sub-sampling and sample preparation	51
2.2.3 Assay	56
2.3 Mineralogical appraisal	57

	page
2.3.1 Thin sections	58
2.3.2 Geoscan studies	60
2.4 Discussion	63
CHAPTER 3 REAGENTS AND ANALYTICAL TECHNIQUES	68
3.1 Preparation and purification of 2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylol phenol (CTMP)	69
3.2 Analytical techniques	73
3.2.1 Boron determination	73
3.2.2 Metal assay	77
3.2.3 Chloride determination	79
3.2.4 CTMP determination	79
3.2.5 Attempted determination of 2-ethyl-1,3-hexanediol (EHD)	82
3.3 Discussion	84
CHAPTER 4 EXTRACTION OF BORON FROM HOMOGENEOUS SOLUTIONS	87
4.1 The choice of systems and methods for study	88
4.2 Apparatus	98
4.3 Investigation of extraction equilibria	109
4.3.1 Effect of contact time and pH	109
4.3.2 Effect of organic concentration	112
4.3.3 Effect of sodium calcium, magnesium and chloride ions	112
4.4 Discussion	116
CHAPTER 5 EXTRACTION FROM SLURRIES	129
5.1 Extraction experiments with synthetic and natural slurries	130

	page
5.1.1 Pulse column experiments in open-circuit	131
5.1.2 Pulse column experiments in partial closed-circuit	134
5.2 Investigation of the clarity of organic phases	136
5.3 Investigation of solvent losses	142
5.4 Discussion and proposals	145
REFERENCES	157

CHAPTER 1
INTRODUCTION

INTRODUCTION

1.1 The borate industry

The average boron content of the earth's crust is of the order of 0.0003-0.001%¹⁻³. Thus the element is scarce and there are few known commercially attractive borate deposits^{2,4}. The formation of such deposits has been the subject of various publications and it is clear that there are three major mineralised belts in the world⁵ from which borates are currently produced. These geological belts are: the Mojave desert area of California, USA; the Alpine Himalaya plateau extending from Turkey through the USSR to Tibet and China; and the high plateau region of the Andes in South America (Fig. 1.1).



Fig. 1.1. Borate minerals occurrences in the world.

The earth's major borate concentrations are formed where magmatic action carries large tonnages of boric acid and borates to the surface by way of volcanoes, geysers, and hot springs^{5,6}. Three essential conditions seem to have governed the formation of rich deposits; the provision of a suitable magmatic source and hydrothermal means of transport; the passage of solutions or vapours through cool or arid regions in which crystallisation is favoured; and the situation of the original deposits in arid or enclosed environments which protect them from dispersion by the elements. In certain cases brines have been formed and have evaporated over geological time to produce interlayered marine sediments containing borates and clays (as in Turkey and Boron, USA^{7,8}). Elsewhere evaporation has led to the formation of concentrated brines^{6,9} containing up to 1.7% borax (as in California, USA). A potential source of boron is seawater which contains about 0.0005% of the element.

Today's borate industry is dominated by five major companies operating in three countries: the USA, Turkey and Argentina. In the USA the major companies are the U.S. Borax and Chemical Corporation (a part of the British RTZ Group), the Kerr-McGee Chemical Corporation, the Stauffer Chemical Corporation, and the Tenneco Oil Company. Argentinian production is 90% controlled by Boroquimica SAMICAF (another RTZ subsidiary) and in Turkey the state-owned organisation Etibank produces most of the country's output.

1.1.1 Reserves of borates

World borate reserves have been quoted^{5,10} as about

8×10^7 tonne of boron content but there is increasing evidence that many times this quantity will become available. Thus in Turkey alone a recent estimate¹¹ gives potential reserves of 10^9 tonne of ore. Table 1.1 shows an updated estimate of reserves country by country.

TABLE 1.1. ESTIMATED BORON RESERVES

Country	Reserves/ 10^6 tonne	Approximate grade/ % B_2O_3
Argentina	3	35
Chile	3	33
Turkey	120^*	40-50
USA	36	25-45
USSR	15	35
Others	3	35
Total	180	
* Estimate based on the potential reserves given by Güney ¹¹		

Argentina has extensive boron mineralisation in desert 'lagunas' in the NW of the country with deposits extending into adjacent territories (Fig. 1.2). Important beds consist of highly deformed sequences of clays and borates containing borax ($Na_2B_4O_7 \cdot 10H_2O$), kernite ($Na_2B_4O_7 \cdot 4H_2O$), ezcurrite ($Na_4B_{10}O_{17} \cdot 7H_2O$), inderite ($Mg_2B_6O_{11} \cdot 15H_2O$ - monoclinic), ulexite ($NaCaB_5O_9 \cdot 8H_2O$) and tincalconite ($Na_2B_4O_7 \cdot 5H_2O$) as the main values¹²⁻¹⁴. The beds underlie the Andes and occur in Chile as ulexite deposits in the Tarapaca region near Bolivian border.

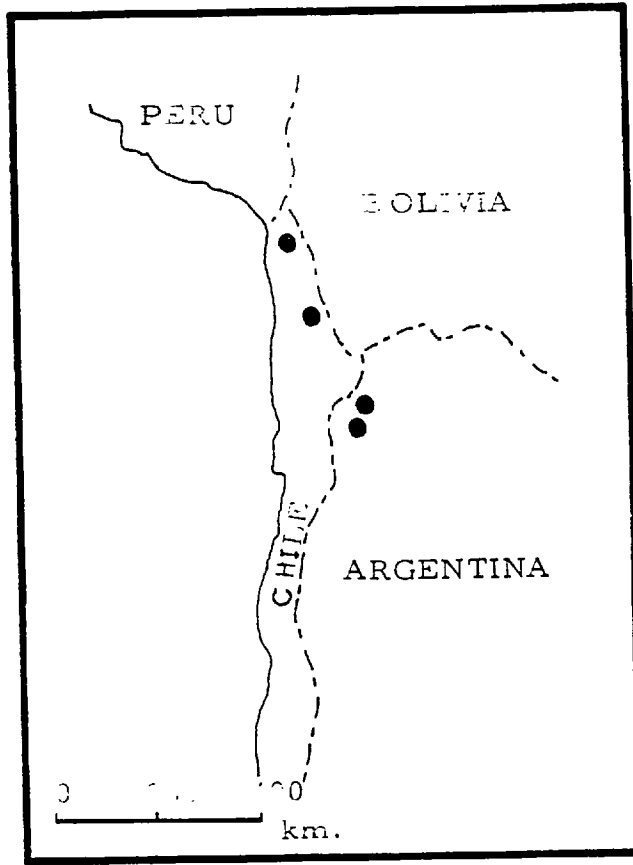


Fig. 1.2. Borate deposits of South America.

The Turkish deposits have yet to be extensively explored but it seems clear that the majority (about 70%¹⁵) of the world's high grade reserves are in that country. The deposits vary widely in mineralogical detail but the majority host rocks are commonly shales, marl, bentonite, tuffs, and limestone, and the mode of formation is chemical precipitation for the boron minerals and sedimentation for

the gangue. These details are considered in more depth in the next section.

Almost all the borate reserves of the United States are in the California desert (Fig. 1.3). The most important deposits are those at Boron in eastern Kern County, at Furnace Creek in Inyo County and at Searles Lake in San Bernardino County in the Mojave desert. The deposits at Boron^{8,16} are thought to have been formed in an early-middle Miocene Lake which was probably fed in part by thermal streams. Borax was deposited in alternating sequences together with montmorillonitic clays and siltstone. The deposits at Searles Lake^{6,9} consist of voids permeated by saturated brines containing hydrated cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} etc.) and anions $[\text{B}(\text{OH})_4^-$, Cl^- , CO_3^{2-} etc.] in association with halite (NaCl), trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), borax, burkite ($2\text{Na}_2\text{CO}_3 \cdot 3\text{Na}_2\text{SO}_4$), etc. The mineralisation here is thought to have formed in Pleistocene times by progressive evaporation of brines in a large catchment area of which the present Searles Lake formed a small part. The Furnace Creek deposits contain ulexite as the primary mineral and colemonite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) as the secondary mineral (thought to have been formed by leaching of the sodium ions from the ulexite^{17,18}). Massive geological faults occur in the area and these have resulted in very irregular mineralisation.

The borate deposits of the USSR are in the Inder Lake district (north of the Caspian Sea); in Kazaklistan; in the Caucasus; and near Lake Baikal. The borate deposits of the Inder Lake district contain ulexite, kurnakovite ($\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$ - triclinic), hydroboracite ($\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$), colemanite, szaibelyite $[\text{Mg}(\text{BO}_2)(\text{OH})]$

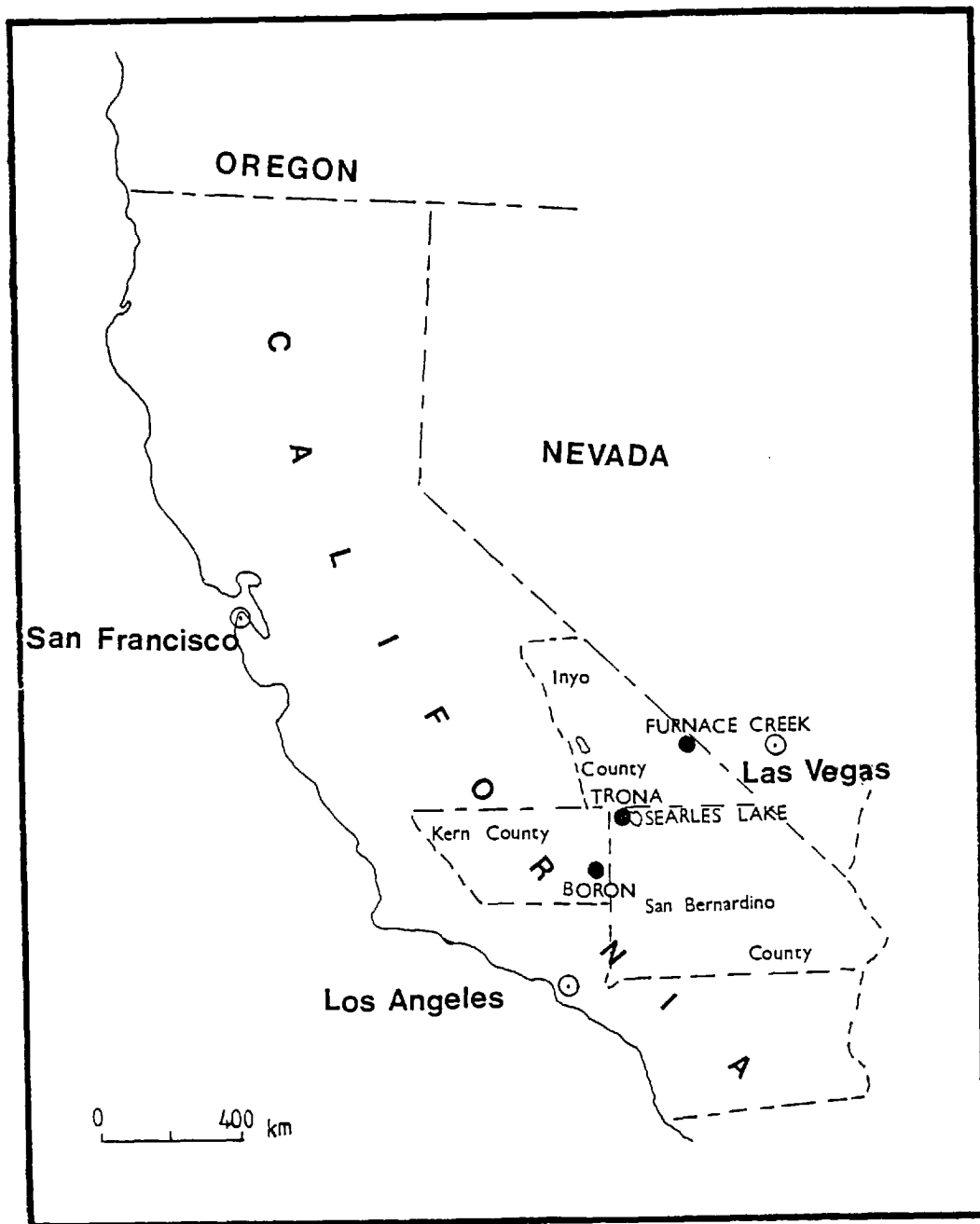


Fig. 1.3. Borate deposits of the U.S.A.

inderite, inyoite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$), etc.¹⁹. In addition to the borate deposits which are thought to have formed in Permian times, the saturated brine permeating the salt bed of the Inder Lake contains small but recoverable amounts of borate together with other salts. Small amounts of borate minerals such as boracite ($\text{Mg}_5\text{B}_{14}\text{O}_{26} \cdot \text{MgCl}_2$) and Luneburgite [$\text{Mg}_3\text{B}_2(\text{OH})_6(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$]²⁰ are recovered from the potash mines such as those of Volga-Ural-Emba Permian salt deposits²¹. The datolite ($2\text{CaO} \cdot \text{H}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$) ores of the Caucasus^{22,23} and tourmaline ($\text{Al}, \text{Mg}, \text{Fe}^{11}, \text{Mn}, \text{Ca}, \text{Na}, \text{K}, \text{Li}, \text{H}, \text{F}, \text{B}, \text{Si}, \text{O}$) deposits of eastern Siberia are of no importance commercially as boron sources.

Of lesser importance at present are occurrences in South-central mainland China²⁴ and northern Tibet which contain a number of semi-dry, boron bearing 'playa' lakes containing moderate amounts of borates; in the Pugga Valley in the Ladakh district of India where there are small deposits recently discovered; in Tuscany²⁵, Italy, where stream vents (soffioni) containing boric acid (H_3BO_3) are found and have been exploited for centuries; and in Germany which has small amounts of borates, boracite, hydroboracite, and szaibelyite (ascharite) recovered from the Stassfurt-type marine potash beds.

1.1.2 Technology

Nowadays the majority of borate production is from open pit mines dealing with solid minerals and/or brines. As most boron minerals are more or less water-soluble most processing methods involve the separation procedures characteristic of solution chemistry.

In some cases sparingly soluble minerals such as colemanite are concentrated by froth flotation. The principal plant flowsheets of the six major American and Turkish companies are briefly explained below (Fig. 1.1).

The U.S. Borax Corporation mines its Kramer ore body at Boron by open pit methods^{26,27}, having converted from underground extraction in 1957. The crushed ore is conveyed to the nearby 80 acre refining plant; leached by water at about 100°C; thickened to remove the bulk of the insoluble material; filtered and precipitated in vacuum crystallisers. Refined decahydrate, pentahydrate and anhydrous borax of various grades, totalling about 4,500 tonne (B_2O_3 content) daily, are produced by repeated recrystallisation, drying, and dehydration processes. High-purity and speciality products are produced at Wilmington, California, and also at Burlington, Iowa.

The Kerr McGee Chemical Corporation employs the evaporative or 'Trona' process at its Trona plant on the shore of Searles Lake²⁸. Potash, borax, di-lithium sodium phosphate, soda ash and sodium sulphate, are separated in sequential stages through crystallisation based upon complex phase-rule chemistry. Some soda ash is recovered through the carbonation process (see below). Solid sodium chloride and waste brines are sent back to the lake. Kerr McGee has a daily B_2O_3 capacity of 300 to 400 tonne (including 150 tonne of anhydrous borax and 80 tonne of boric acid) and processes 7.5 m^3 per second of brine pumped from a series of wells.

Stauffer Chemicals²⁹ West End plant (a subsidiary of

Kerr McGee since 1974) employs the carbonation process whereby carbon dioxide (from calcining limestone) is used to remove sodium hydrogen carbonate and soda ash. The filtrate is blended with the additional raw brine and sent to vacuum crystallisers to obtain borax decahydrate, borax pentahydrate and anhydrous borax. Brine intake is about 3 m^3 per second. Daily capacities are 350 tonne of soda ash, 200 tonne of equivalent decahydrates, 450 tonne of sodium sulphate.

American Potash and Chemical Corporation^{30,31} has developed a method in which soluble borate in brines or weak plant-end liquors is recovered as a boron-organic complex. The solution of borate is first treated with a kerosene solution of a special polyol, which sequesters (complexes) the borate, later to be released as boric acid on stripping with sulphuric acid (see Section 1.3).

Tenneco Oil Company's colemanite-ulexite open pits at Ryan¹⁰, California, supply colemanite ore to a calcining plant near Death Valley Junction, and ulexite to a mill at Dunn for upgrading to 26 - 28% B_2O_3 . Colemanite is calcined to raise the B_2O_3 content from about 22% to 48%.

The Hisarcik open pit colemanite mine in the Emet district of Turkey was recently converted from a hand-sorting to a more modern mode of operation. The new washing and screening plant is rated at 660,000 tonne per year of feed (28% B_2O_3) and 330,000 tonne per year of product (43% B_2O_3). Mining is partly mechanized.

The open pit borax deposits at Kırka (Eskisehir province of Turkey) are being developed in a systematic manner to provide 26

to 27% B_2O_3 ore for a washing plant rated at 440,000 tonne per year of upgraded concentrate. Etibank is constructing a refinery at Kırka designed to accept a feed from this washing plant containing 35% B_2O_3 . The plant which is similar to the U.S. Borax refinery at Boron, will produce annually 200,000 tonne of crude pentahydrate borax, 55,000 tonne of crude anhydrous borax, and 11,000 tonne of refined anhydrous borax. Presently the washed ore is trucked to a smaller refinery at Bandırma (on the Marmara Sea) which has a yearly capacity of 60,000 tonne of borax and 28,000 tonne of boric acid.

Elemental boron^{30,32} may be produced by several processes including reduction of boric oxide by magnesium metal, fusion with metal salts, vacuum fusion, vapour phase reduction of a volatile boron compound, or high temperature reduction of boron trichloride by hydrogen. The latter is receiving great attention and it may replace the industrial methods presently used to produce elemental boron.

Most of the beneficiation methods presently used to evaluate borate ores are conventional but as new industrial uses of borate minerals are developed, and hence the consumption increased, there will be a need to recover boron from plant-end liquors, natural brines, etc. and thus more sophisticated methods of treating boron minerals, such as solvent extraction, will emerge to replace the conventional ones. Moreover, when pollution is taken into account chemical treatment of the plant-end liquors will dominate the technology.

1.1.3 Uses

The commercial uses of borates and their derivatives are both wide and varied, and these materials have been described as the most versatile intermediate chemicals in the manufacturing industry³. Depending upon the form and quantity in which boron minerals are used a wide diversity of properties may be exhibited and put to use. For example, specific borates can be used both for explosives and flame-proofing, and both as fertilizers and as herbicides. Figure 1.4 summarises the industrial uses of borates and their derivatives.

The main consumer of borates, on a quantity basis, is the glass industry. Anhydrous borax is used in 'Pyrex' glass and in glass-fibre, the latter becoming increasingly important as an insulating material as the need to conserve energy increases worldwide. Glass fibre is also of increasing importance as a reinforcing material (in the textile industry) and as a strong lightweight construction material. Borax, decahydrate, is a commonly used flux for glazes on ceramic bodies and is also widely used in enamels and as a water 'sweetner'. Sodium perborates are employed as water softeners in domestic washing powders.

To a varying degree boron is an essential nutrient to many plants but is toxic at concentrations greater than about 5 ppm depending upon the species^{33,34}. Boron minerals are employed therefore both in commercial growth regulators (fertilizers) and in inhibitors (herbicides)³⁵. Borates are also of value in photography, as insecticides in starch pastes, as fire-retardants, as fluxes for brazing and welding,

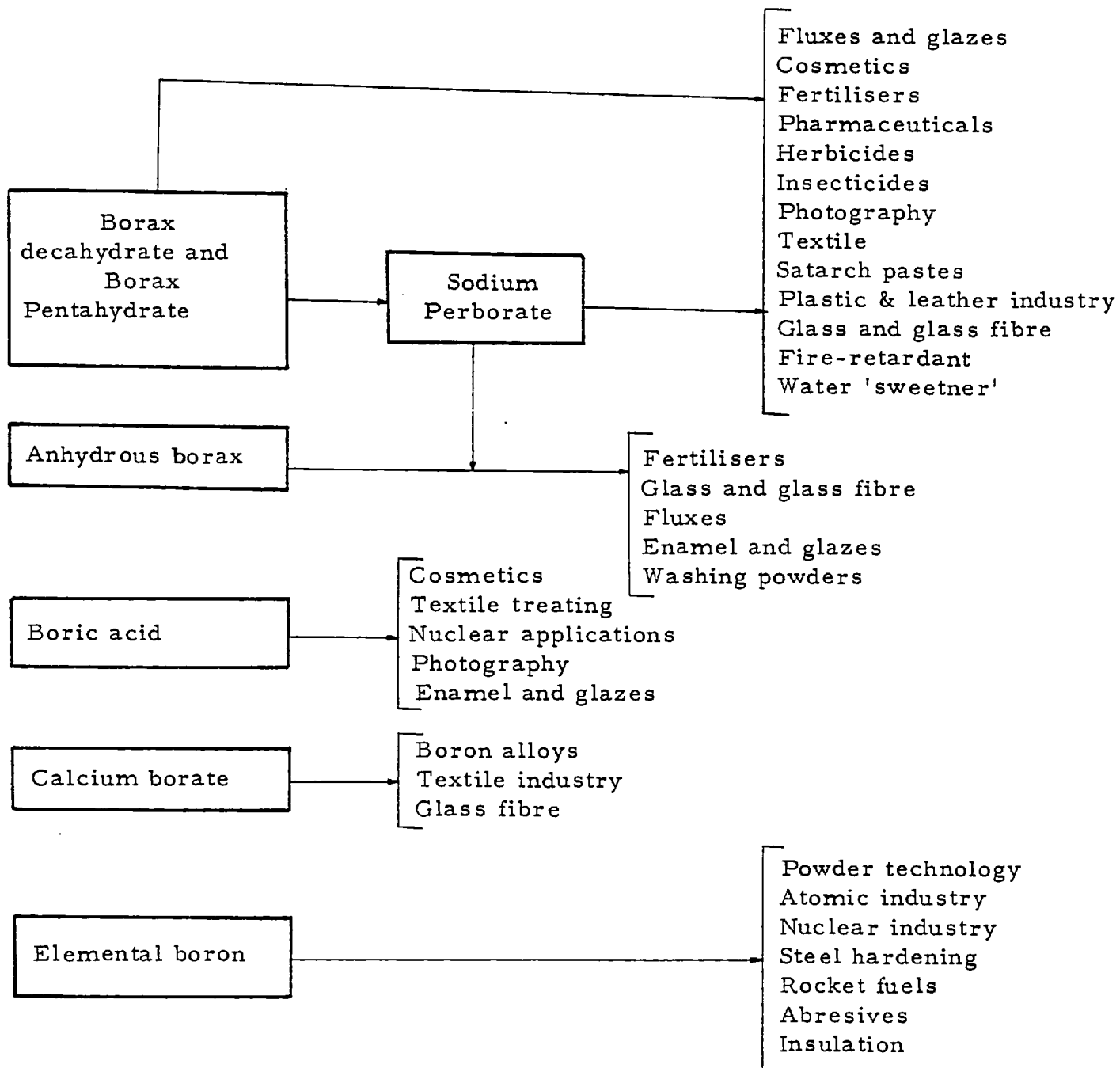


Fig. 1.4. Industrial uses of boron compounds.

in the manufacture of paint and paper, as a buffer in plastics manufacture, in leather processing, in cosmetics and pharmaceuticals, etc.

The four simple compounds borax, boric acid, calcium borate, and sodium perborate account for at least 80% of total consumption, but other materials are becoming of increasing importance. The utilization of the special properties of elemental boron and certain of its compounds have been extensively studied by the military and industry³⁶. Elemental boron³⁷ has the unique property of absorbing neutrons produced by nuclear reactions without the emission of secondary gamma radiation, and is used for this purpose (the B^{10} isotope) to protect personnel from the harmful effects of nuclear reactors. Ultrafine metallic boron finds applications in powder technology and in steel-making to improve the effect of other hardening elements, such as carbon. In the process known as 'boronising', boron gives steel a super-hard surface^{38,39}. Boron fibre is increasingly used to reinforce plastics and metals for the manufacture of products such as aircraft wings and helicopter rotors. Boron carbide³⁸ is the third hardest substance known and has an unusually high strength-to-weight ratio which makes it ideal as a ceramic armour in aircraft and similar constructions. The even harder boron nitride^{41,42} has the ability to resist chemical attack by molten metals. It is extensively used as a high temperature electric insulator and as a thermal conductor.

During the last few years boron, in the form of boron hydrides^{43,44}, such as diborane (B_2H_6), pentaborane (B_5H_9), and decaborane ($B_{10}H_{14}$) has become an important additive in rocket fuels.

Borates are listed as important strategic minerals for their newly developed use as organoboron compounds in anti-knock agents for petrol. Because metallic oxides are soluble in molten borax, it has been tested as a substitute for flourspar fluxes in steel making processes, especially in basic oxygen furnaces. New and diversified applications of boron compounds are being developed every year by research organisations such as Borax Consolidated UK Ltd. (Chessington, Surrey) and it is clear that demand will increase.

1.1.4 Marketing

The three major boron producing countries in the western world, the USA, Turkey and Argentina, export a large proportion of their production (Fig. 1.5). Exports from Argentina are confined to the LAFTA (Latin America Free Trade Area) countries¹³, particularly Brazil, which also imports large tonnages of borates and boric acid from the USA. The bulk of exports from the USA⁴⁵ enters Europe via Rotterdam, where special port facilities have been constructed for the efficient handling of these products. Rotterdam acts as a mediator port in distributing borates throughout Europe. The larger share of this trade goes to West Germany, France and the UK which together take nearly 60% of the total, with Italy, Belgium and Luxemburg taking a further 20%. US exports, other than to Europe, are mainly confined to Japan, Canada and South America. Japan takes about 30% of the US exports of boric acid and over a quarter of the sodium borates. Canada and Mexico together take about an eighth of the refined borates and just under a quarter of the boric acid.

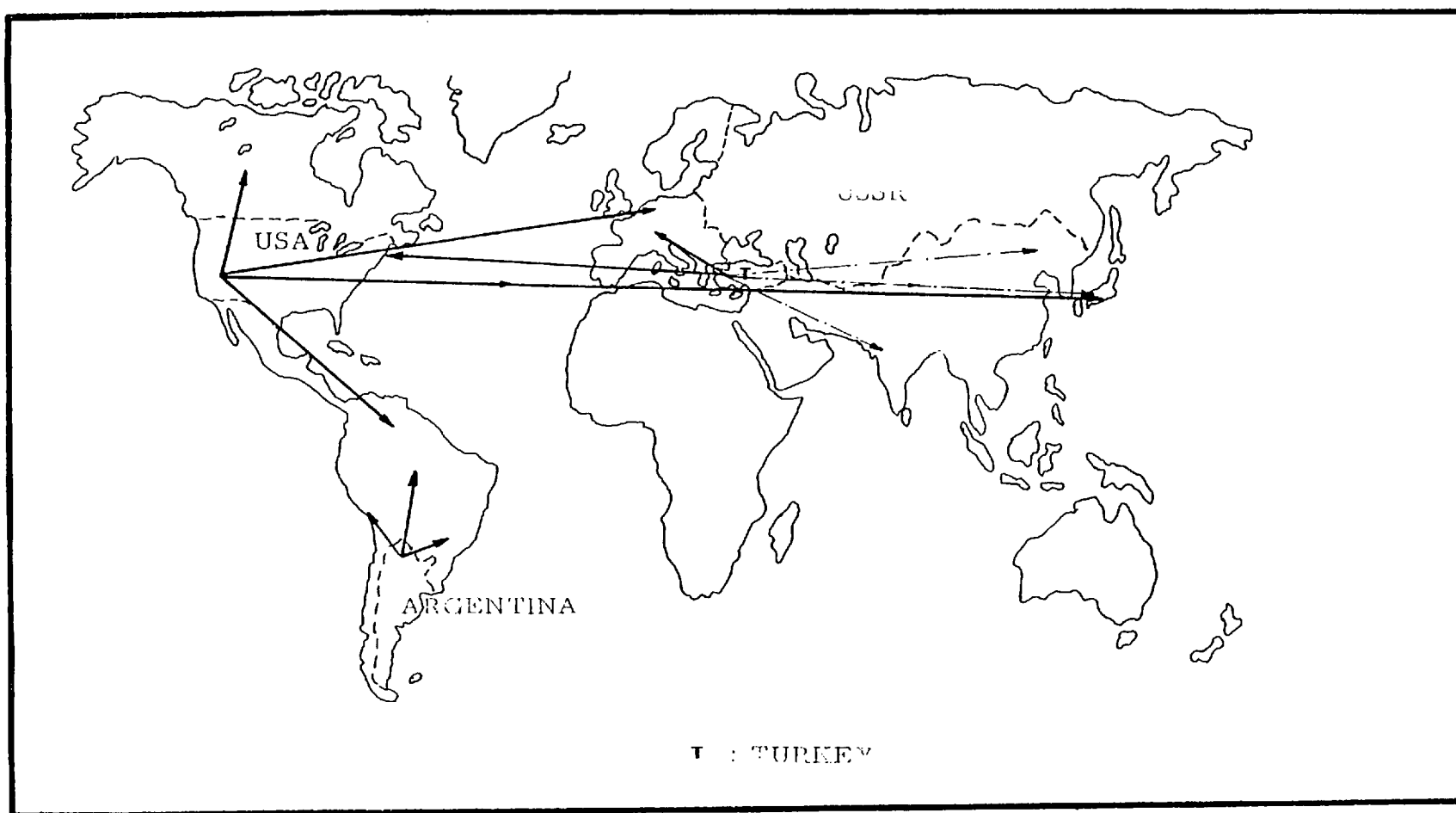


Fig. 1.1. Marketing of borate minerals.

A number of consumers in Europe have direct links with Turkey which supply them with boron products¹⁵. In 1972, Italy took 85,000 tonne of borates from Turkey and 20,000 tonne from the USA, France imported 43,000 tonne from Turkey and 61,000 tonne from the USA, and West Germany took 64,000 tonne from Turkey and 97,000 tonne from the USA. The output of the borax and boric acid plant at Bandirma (which is run by the Etibank Co.) is mainly shipped to European markets, but new markets are opening up in the Near and Far East, especially in Pakistan, India, Japan and China. Turkey also supplies European markets with colemanite, ulexite and boron raw materials to be used in fibre-glass, steel and other industries.

1.1.5 Prices

From 1954 to 1973 world production and consumption of borates nearly tripled, whereas real prices were cut by roughly 50%¹⁰, owing in part to steady improvements in plant operating efficiencies. However, in 1974, the price of anhydrous products rose by about 85% and the prices for hydrated products rose by about 23%⁴⁶. These prices reflect steep rises in energy costs, inflation and strong demand. The sharper rise in the costs of anhydrous products, compared with hydrated products may be explained by the more intensive use of energy in producing the former. This fact has also caused producers to shift part of their anhydrous production to hydrated products. From the end of 1975 onwards the production of borates has become firmer, prices have remained almost steady, and demand has steadily increased.

1.1.6 Future of the borate industry

The increased use of borates in the glass industry for constructional and insulation purposes (the likely average growth rate is 5.7% per year to the year 2000¹⁰), will probably tend to push borate demand to a higher level, because the glass industry accounts for about $\frac{1}{3}$ of the total demand for borates. Also the use of boron-containing specialised materials in fuels should expand at a high rate. On the other hand, growth in demand may be reduced by the fact that some degree of substitution of borates by other metals may be possible in the detergent and agricultural industries⁴⁷.

Continued growth in demand should be assisted since borates may be used as substitutes for a number of conventional minerals, for example, they can be used in place of flourspar in steel-making. Despite the limited number of known commercial deposits, reserves (estimated at 80 m tonne⁵) appear to be adequate to fulfil the likely demands well into the next century.

1.2 Turkish boron industry

Little has appeared in the English language recently concerned with reviewing in detail the Turkish boron industry. Part of the survey below results from two extended visits to Turkey during 1976/1977.

All the known borate deposits of Turkey are situated in Western Anatolia (Fig. 1.6). The first exploration and authenticated working of boron minerals was begun in Sultancayir district (Balıkesir)

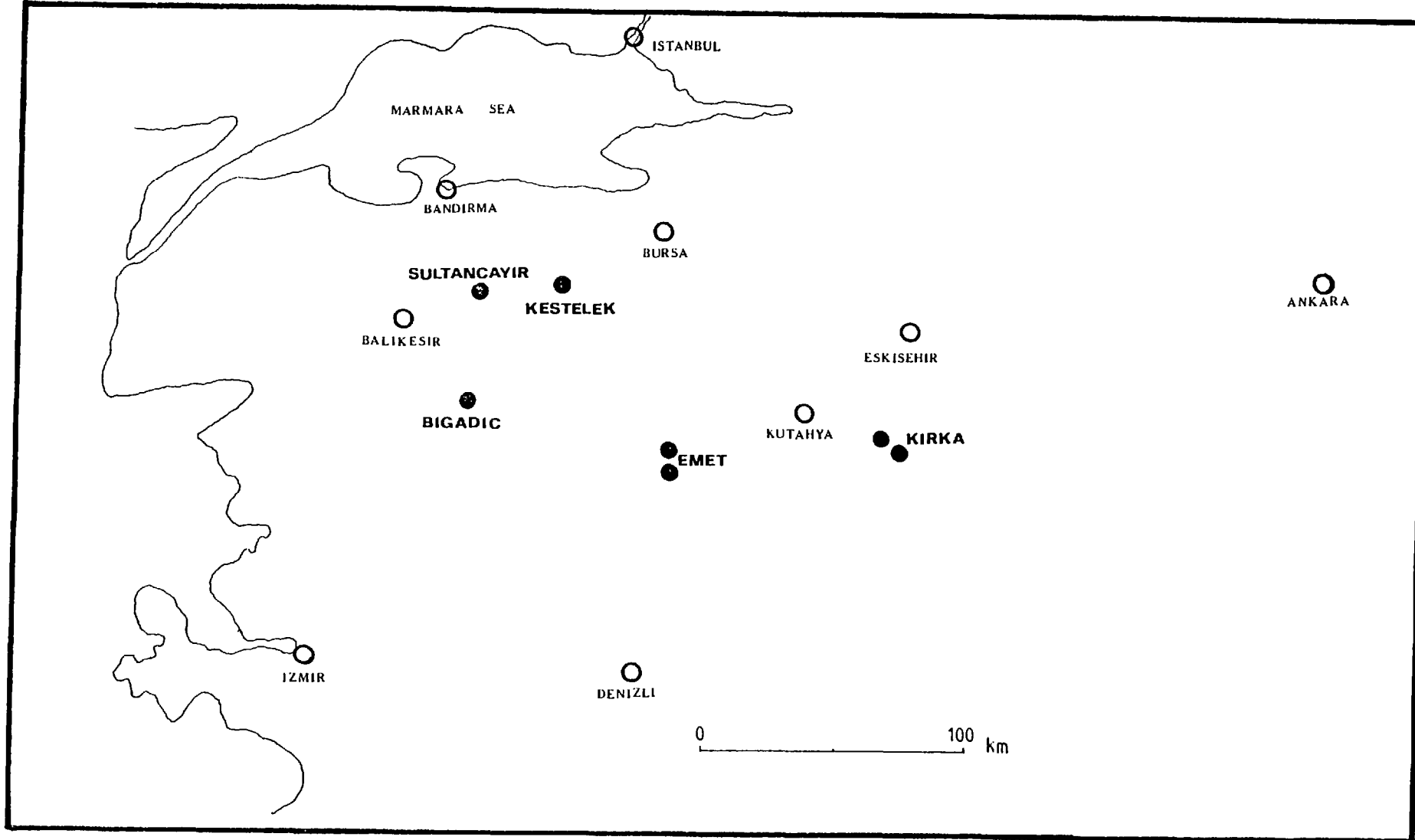


Fig. 1.6. Borate deposits of Turkey.

in 1965 by the French Campagnie Industrielle de Mazures¹⁵, although there is some evidence of Roman workings in that area. Pricerite, the main mineral in Sultancayir, remained the most important source of boron until the deposits became exhausted in 1954. In the early 1950's, other deposits were discovered which were to lay the foundation of the modern Turkish industry. These included large beds of colemanite at Bigadic (1950), Bursa (1952) and Emet (1956). In the late 1960's, Maden Tetkik ve Arama Enstitüsü - M. T. A. (The Mining Research and Exploration Institute of Turkey) working on behalf of the Etibank Corporation (a government owned mining company) carried out an extensive exploration programme in the Sarayköy (Kirka) locality which blocked-out a large potential borax deposit⁷. These finds and the results of more recent intensive exploration indicate that some 70%⁴⁸ of the known world boron reserves are situated in Turkey.

1.2.1 Geology and formation of the deposits

As with most borate deposits, those in Turkey are essentially volcanic/evaporite in origin, the most commonly occurring minerals being pricerite (Sultancayir), colemanite (Bigadic, Kestelek and Emet) and borax (Kirka). It seems clear that the deposits were all formed from similar volcanic sources at almost the same geological time⁴⁹⁻⁵¹. Thus the mineralisation is generally classified as occurring in Lacustrine facies of the Upper Tertiary period (65 m. years ago) and is usually associated with interlayered tuffs and clay/marl series.

The precise locations of the volcanic sources are not known but as the five major deposits are all at least 40 km apart, the simplest assumption is that there were five separate volcanic sources. To give

a simplified picture, the following geochemical processes can be envisaged to have occurred:

- (1) Magmatic/hydrothermal transport to the surface of boron rich material such as boric acid.
- (2) Water transport to an inland depression where evaporation, sedimentation and crystallisation could occur.
- (3) Phase zoning according to the relative solubilities of the chemical species present, both as a result of incoming solutions/suspensions and in situ hydrolysis of any pyroclastic material.
- (4) Burial of the beds under younger sediments and partial alteration of the original formations to give secondary (metamorphic) series.

The most closely studied Turkish deposit is that at Kirka, and it is believed to have been formed more or less as suggested above. The predominant species present originally being sodium ions and borate ions (Fig. 1.7). A detailed geological study of this region has been

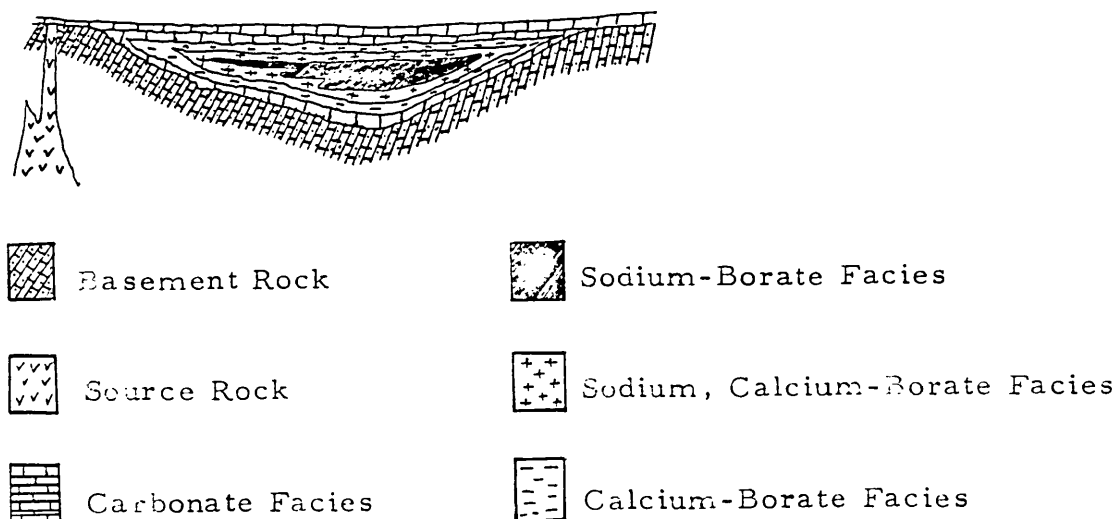


Fig. 1.7. A schematic section through the Kirka deposit.

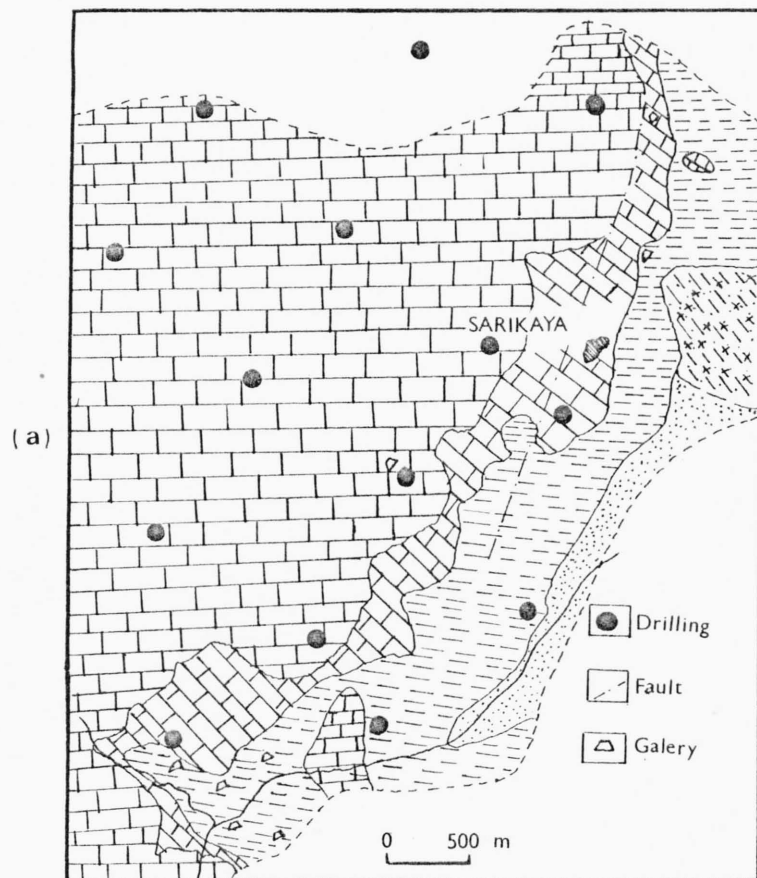
undertaken⁵² and the interlayering of minerals found (Fig. 1.8)^{52,53} explained in terms of a semi-quantitative phase diagram discussed in Chapter 2.

The other deposits are predominantly calcium borates and although they do not contain a large proportion of borax, their mode of formation is likely to have been similar to that at Kirka. The major discriminating factors seem to have been the ratio of $\text{Ca}^{2+} : \text{Mg}^{2+} : \text{Na}^{+}$ and $\text{B}_4\text{O}_7^{2-} : \text{CO}_3^{2-}$ in the primordial solutions. It is reasonable to assume that calcium carbonate would precipitate preferentially as this compound has the lowest solubility product, and that the proportions of other ions would thereby increase in such a way that inyoite, inderite, ulexite and borax would tend to precipitate sequentially thereafter. As the solid minerals found first will be highly hydrated, it is expected that burial and marginal heating will cause dehydration, recrystallisation and even leaching out of soluble sodium ions to give a series of secondary minerals. These ideas are explained in a Turkish paper by Baysal⁵³.

With the exception of that at Kirka, the Turkish deposits contain mostly secondary minerals such as pricerite and colemanite. It should be noted however, that the number of possible phases containing boron is very large and that some 15 such minerals have been identified in the Anatolia region.

1.2.2 Turkish mine sites

As described briefly and illustrated earlier (Fig. 1.6), there



(b)

GEOLOGICAL		Thickness/m	Lithology	DESCRIPTION
ERA	Period			
		?		River sediments
CENOZOIC	Tertiary	?	b b b	Basalt
		?		Upper limestone with cert layers
		60		Upper clay, marl, tuffs, coal bands
		70		Borate zone, clay
		40		Lower clay, marl, tuffs
		80		Lower limestone
		80		Tuffs
		?		Eocene limestone, conglomerate
PALEOZOIC		?		Schists

Fig. 1.8. (a) Geological map of Kirka

54

and (b)

Generalised stratigraphic and geological column of Kirka

are five borate mining districts in Turkey: Sultancayir, Bigadic, Bursa, Emet and Kirka. The first three are rather small privately-owned operations engaged mainly in mining and selling ore with little or no processing or concentration, and marketing their products directly in Europe. Until 1969, Borax Consolidated (UK) Ltd. had a controlling interest in several of these mines but following expropriation in that year their holdings were greatly reduced. Typically, Bigadic region supports twelve mines operated by five companies namely, Turk Boraks Madencilik Company, Mortas/Bortas Group, Rasih and Ihsan Corporation, Ali Sayakci and Yakal Borasit Ltd. and Kemad Corporation, which have total reserves of at least 8 million tonne $(40\% \text{ B}_2\text{O}_3)^{54}$ and are worked on such a small scale (400 - 40,000 tonne per annum) that mining can continue into the foreseeable future. There is little tendency to develop or expand operations here, but it is likely that the companies will be nationalised in due course.

Emet and Kirka mines are both state-owned (Etibank Corporation) and are operated on a much larger scale. In the former case, some 40 million tonne $(40\% \text{ B}_2\text{O}_3)$ of colemanite is available in the form of nodules of 10-40 cm. diameter, associated with small quantities of other minerals such as soft tuffs and clays, calcite and arsenic sulfides (Realgar: As_2S_2 , and Orpiment: As_2S_3). Both open pit and underground methods are used and until 1973 the processing method was hand-combing. In that year construction of a new concentrator was completed designed to process 600,000 tonne per annum of $26\% \text{ B}_2\text{O}_3$ ore. The ore is processed in two sections relying on the softness of the gangue constituents. In the first crushing and screening produces

a coarse dry concentrate and a finer clay-rich fraction, while in the second a fine-sized concentrate is produced by water scrubbing the clay-rich fraction.

At Kirka the total ore reserves (mainly borax) suitable for open pit operation are estimated to be 500 million tonne . The average overburden is about 60 m. thick⁵⁵. The plant employs a wet-concentration method (Fig. 1.9) and operates as a washery on 100 tonne per hour dry feed with an average head grade of 26-27% B_2O_3 . It produces concentrate at an average grade of 34% B_2O_3 at the rate of 67 tonne per hour. This flowsheet is considered in more detail in Chapter 2.

Etibank's boric acid plant at Bandirma started production in 1969 with the relatively small capacity of only 6,000 tonne per annum boric acid and 20,000 tonne of refined borax, but with improvements in the processing plant at Emet and the start of the processing plant at Kirka (1974), the capacity was increased in 1975 to 28,000 tonne per annum boric acid and 60,000 tonne of refined borax. Etibank has announced (1978) that it is to construct a boric acid plant of 100,000 tonne per annum at Bandirma with a completion date in 1979. Furthermore, a new plant is under construction at Kirka designed to produce 200,000 tonne of crude pentahydrate borax, 55,000 tonne of crude anhydrous borax, 11,000 tonne of refined anhydrous borax and 15,500 tonne of refined decahydrate borax annually. The company is expanding its storage and handling facilities at the port at Bandirma through which most of its products are exported.

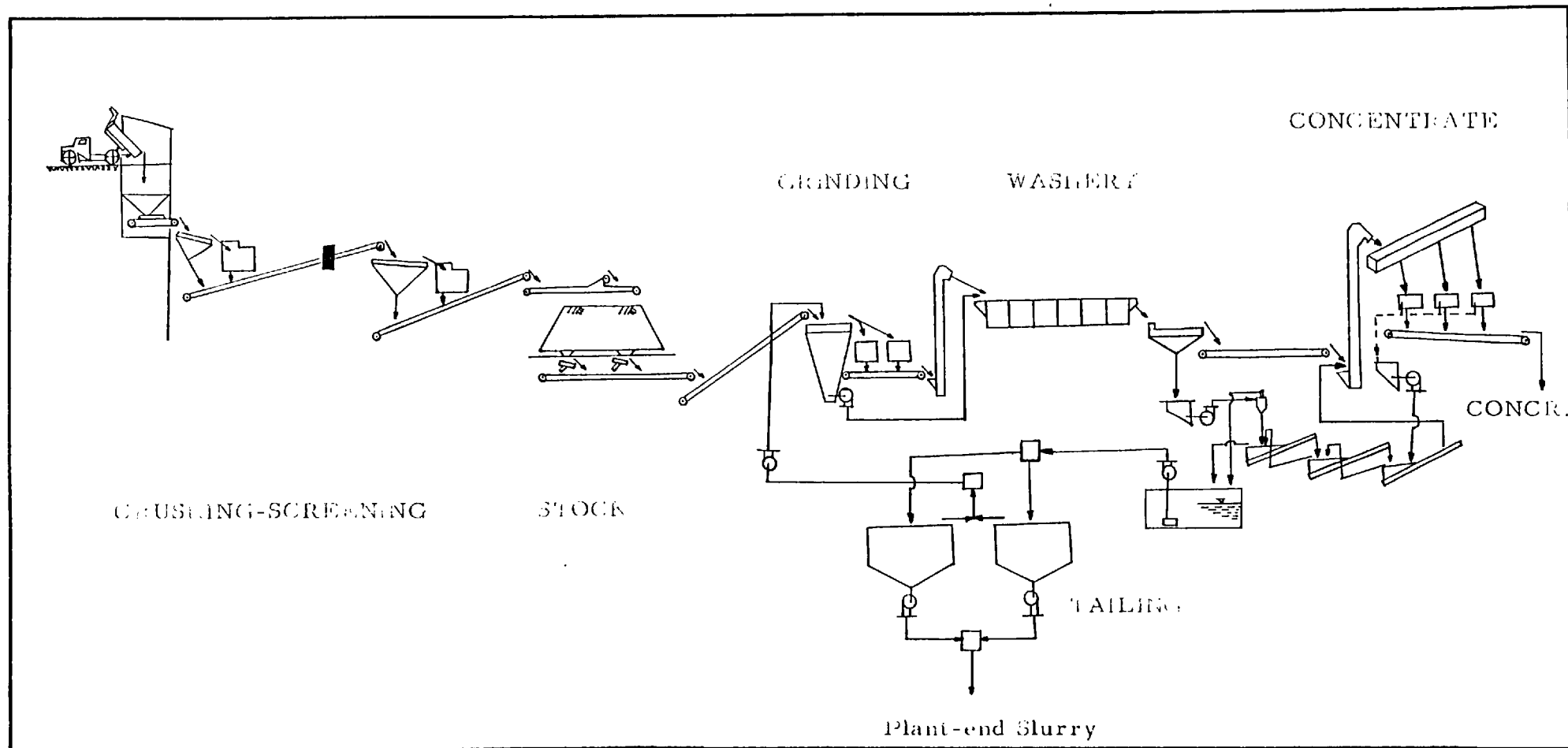


Fig. 1.9. Flowsheet of Kirta operation.

The output of boron minerals from both state and private enterprises exceeded one million tonne in 1976. Production of boron minerals in Turkey between 1970 and 1976 is outlined in Table 1.2^{46,47}.

TABLE 1.2. TURKISH BORATE MINERALS PRODUCTION

Year	Annual Production in Tonne
1970	522,930
1971	609,200
1972	622,400
1973	625,600
1974	1,080,500
1975	970,900
1976	1,040,000

As can be seen, there was a significant increase in 1974 resulting from the impact of the start up at Kirka, and similar increases are expected in the next few years.

1.2.3 Markets and future outlook

Turkey supplies about 40% of the world requirement for borate minerals¹⁵, and in view of the large reserves (Table 1.3) this situation can be maintained indefinitely providing the markets are not lost. In fact it is expected that Turkey's share of the market will steadily increase.

Internal consumption, however, is less than 5% of the output. The main borate minerals consuming industries in Turkey are these producing washing powders, enamels and pharmaceuticals, which the cosmetic and glass industries consume smaller quantities.

TABLE 1.3. ESTIMATED BORATE RESERVES IN TURKEY¹⁵

District	Known Res/ 10 ⁴ tonne	Potential Res/ 10 ⁴ tonne	Total Res/ 10 ⁴ tonne.	Av. Grade %B ₂ O ₃	Res. B ₂ O ₃ Content/tonne
Bigadic	470	31	780	40	3120
Bursa	5	0.8	13	40	52
Emet	1514	225	3764	40	15056
Kirka	1211	4020	41411	30	124233
Total	3200	42768	45968		142461

1.3 Recent developments

Four areas require consideration in this context: new deposits or other sources of the element; new processing methods; new uses; and improved environmental control. Development of new sources of boron is less important than hitherto because of the large discoveries made in recent years. Various estimates show that present reserves are adequate for world needs well into the next century⁵. New uses of boron commodities are constantly being sought and some of these have been discussed in Section 1.1.3. Thus considerations here are restricted to the newer processing methods and prospects for

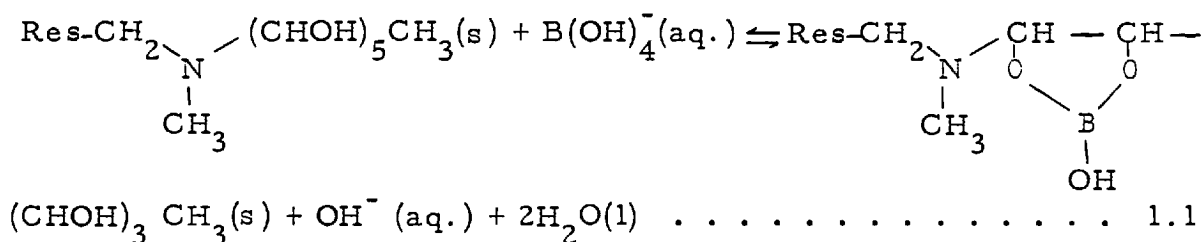
better environmental control. In common with much development work in metallurgy, the main emphasis is placed on careful integration of unit operations and reduction in the impact of obnoxious effluents.

Processing methods for boron ores are dominated by the ready solubility of most of the minerals of interest, and thus the major developments in the past have been in the field of solution chemistry. There has been relatively little work concerned with conventional physical and flotation concentration methods which at present are rarely used in the industry. A number of papers have appeared recently however: thus, a Soviet report⁵⁶ considered the possibility of neutron activation of liberated boron-silicate minerals (such as datolites, $2\text{CaO} \cdot \text{H}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$) followed by separation on a 1-channel band separator; and several workers reports investigations aimed at beneficiating boric acid and colemanite by flotation⁵⁷⁻⁵⁹ using petroleum sulphanates - replacement of a hydrogen atom by sulphonic acid SO_3H - (R-825 and R-840) and Pale oil sulphonate as flotation reagents.

The dissolution of boron minerals in water or dilute mineral acids is relatively straightforward and rates and extents of solution have been known for a long period of time^{60, 61}. Nevertheless, reports occasionally appear concerned with alternative methods, one example being that concerned with leaching datolite ores with carbonic acid solutions⁶².

Major recent developments have shown the way to producing purer commodities, particularly through ion-exchange and solvent extraction techniques. Use of these techniques has the considerable

advantage of avoiding the more traditional and tedious procedures of fractional crystallisation. Various reports in the literature describe so-called boron specific anion exchange resins although they are not yet used commercially. A patent covering the use of such resins (cross-linked copolymers of styrene and divinylbenzene having attached to their aromatic nuclei groups of the structure $-\text{CH}_2\text{N}(\text{CH}_3) \text{C}_6\text{H}_8(\text{OH})_5$) has been published⁶³. It is assumed that an equilibrium of the following type is involved in the exchange:

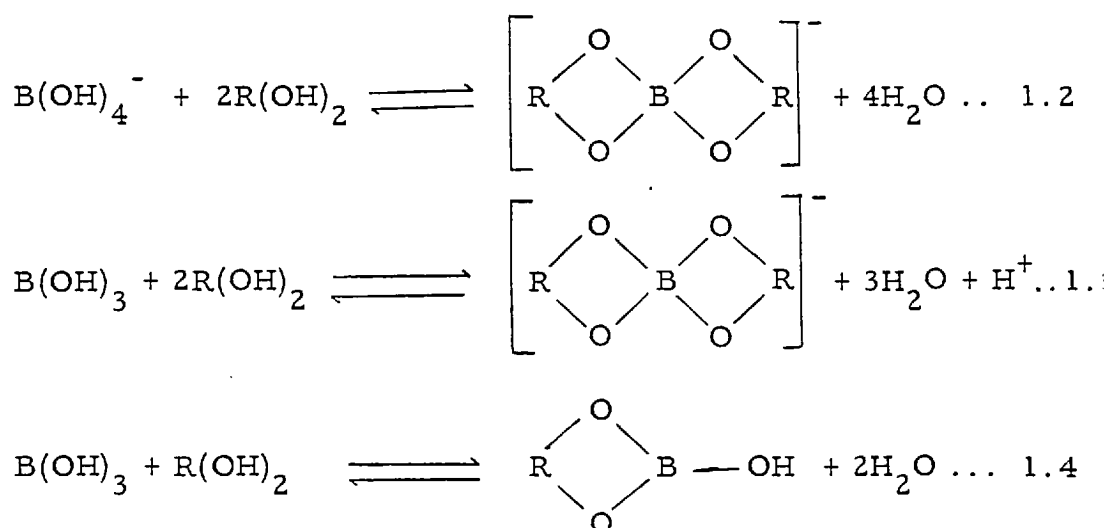


Rohm and Haas (UK Ltd.) market a boron specific resin (Amberlite XE-243)⁶⁴ which is assumed to have similar chemistry. Other published work includes studies by Grekovich and Materova⁶⁵ on the absorption of boric acid by anion exchangers saturated with the anions of certain hydroxy-acids, and absorption of various sugars onto anion exchangers in the borate-form. Despite these developments, solvent extraction is of far more importance industrially at the present time.

In 1963 the American Potash and Chemical Corporation constructed a plant for concentrating boron species from brines at Searles Lake (California) by means of solvent extraction into kerosene containing proprietary polyols^{31,66,176}. Arnold¹⁷⁷ has given some process control details of this plant and a representative flowsheet⁶⁷

is given in Fig. 1.10. In general terms, the plant is operated as follows. Brines from the lake (containing only 1.7% sodium borates) together with plant-end liquors from the evaporation-crystallisation process are contacted with a kerosene solution of a polyol (the name is not disclosed) in multistage counter current mixer-settlers. Boron is released from the loaded organic phase by stripping with dilute sulphuric acid in similar equipment. Carbon treatment of the strip liquor to remove organic materials is undertaken in a semi-continuous column, and the resulting clarified acidic solution is sent to two evaporator-crystallisers. The first of these separates boric acid, and the second a mixture of sodium and potassium sulphates, according to the respective solubilities. Boric acid of about 99.9% purity is produced.

The method is successful in selectively removing borate and boric acid from the complex solutions of different ions which exist in the brine because of the tendency of the former species alone to form stable complexes with 1,2 and 1,3 organic diols. Reactions of the type outlined in equations 1.2-1.4 may be taken as representative^{68,69}.



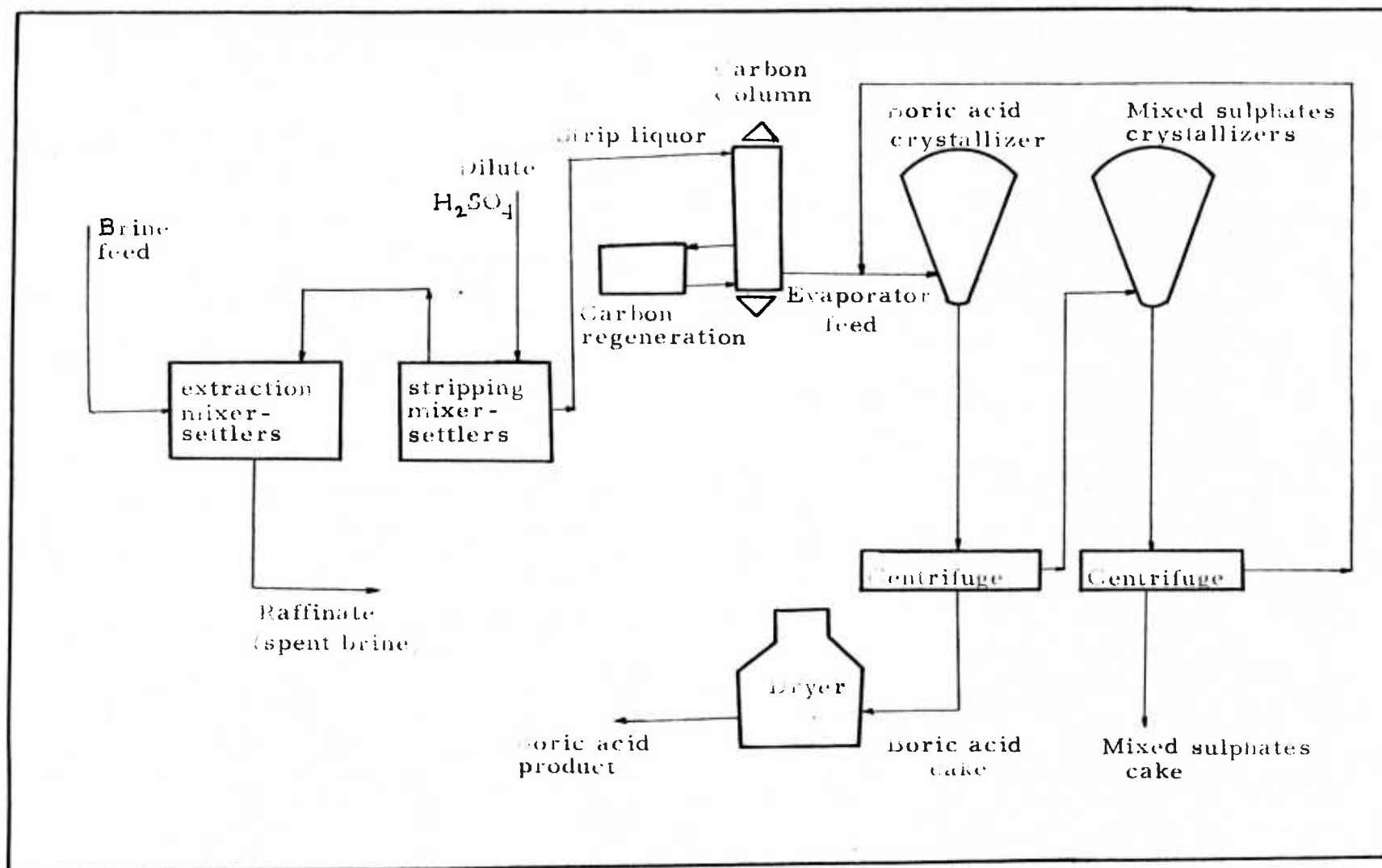


Fig. 1.10. Schematic flowsheet of Searles Lake solvent extraction plant⁶⁷.

In these equations R is meant to be an aromatic and/or aliphatic hydrocarbon chain. Depending upon the nature of this chain, the boron-organic complexes formed contain either 5 or 6 membered rings.

Boron can cause an environmental hazard. Although at low concentrations, it is an essential plant nutrient as mentioned earlier, the element is toxic to many plants at concentrations above 4-5 ppm depending upon species³³⁻³⁵. Attempts are therefore being made to reduce any hazard to agriculture likely to result from boron containing mine or plant effluents. This problem is beginning to reach significant proportions in Turkey where there is a danger at least of three large scale operations of causing severe pollution in the not too distant future. Thus, at the Bandirma boric acid plant, effluent averaging 14% B_2O_3 is discharged directly into the Marmara Sea (Fig. 1.11) at the rate of almost 30,000 tonne per annum, and must be causing a significant build-up of the boron concentration in that enclosed volume of water⁷⁰. Additionally, the effluent contains suspended fine clay and gypsum particles. Work at the Marmara Arastirma Enstitusu - MAE (Marmara Research Institute) in Gebze-Kocaeli, forty miles from Istanbul, is in progress in an attempt to develop processes firstly for removing particulate matter and secondly for reducing the boron content (by solvent extraction) in the clarified solutions from the plant⁷¹.

At the Emet colemanite mine serious pollution is possible from the boron and arsenic-rich effluents from the washeries, which contain about 16% B_2O_3 and 25-30% solids⁷². The mine and tailings facility is situated on a steeply sloping site overlooking extensive



Fig. 1.11. Point of discharge of boron-rich effluent from boric acid plant (Bandirma) to Marmara Sea.

agricultural land, and the tailings pond is currently too small to permit full production rates without allowing effluent to escape into the local irrigation system. Thus production must be restricted while the pond is extended. Although pollution does not yet cause serious problems at the Kirka plant, the situation could easily deteriorate as at Emet, and clearly deserves careful planning as soon as possible. This matter is under consideration by the Etibank Company⁷³.

Further south at Saraykoy-Denizli, wells have been drilled to produce steam to run a pilot 20 MW power station (Fig. 1.12). A problem arises, however, because the run-off water contains high levels of boron and other minerals which also find their way into nearby irrigation channels. No solution has yet been found which will permit an environmentally safe full-scale station to be constructed, but

reinjection has been considered as a possibility by the operating company (MTA)⁷⁴.



Fig. 1.12. Natural boron-containing steam wells at Saraykoy Denizli.

It is evident that solvent extraction and/or ion-exchange could be of importance in overcoming these problems in future years, provided the necessary research and development work is undertaken.

1.4 Aims of the present work

The foregoing discussion has shown that an environmental hazard is likely to develop from boron containing effluents and that purification of plant-end liquors by either solid or liquid ion-exchange offers a possible means to counteract this situation. Such a means must be particularly constrained economically because the borate deposits are high grade and large, and therefore little or no significant revenue can be expected from the marginal extra production obtained by reducing boron levels in effluents. It is therefore very necessary to investigate all ways of reducing likely costs. Probably the most obvious way to overcome the problem (other than by permanent containment) is to contact effluents directly with a solid or liquid ion exchanger and to discharge barren pulps to the drainage system.

There is no information available in the literature at present on resin-in-pulp or solvent extraction-in-pulp methods for borate liquors, and the main aim of the present work is to carry out fundamental studies in this area with particular reference to the problems arising in Turkey. Subsidiary aims fall naturally into four groups. The first of these is to present a general review of borates as commodities (Chapter 1). An in-depth study of the mineralogy and/or chemistry of relevant ores, effluents and reagents forms the second group (Chapters 2 and 3). The third group deals with the elucidation of the chemistry of exchange reactions on clear 'synthetic' solutions - that is without the presence of interfering effects from particulate matter (Chapter 4) and the fourth group deals with analogous processes on pulps (Chapter 5).

In order to make the best use of available time and resources it was necessary to make a choice between solid and liquid ion-exchange for the study. The choice was not clearcut because both the methods have a series of merits and disadvantages in their applications to aqueous processing generally, and each is the subject of considerable uncertainty in the literature, particularly when aqueous pulps are involved. Thus, it is stated that resin ion-exchange is more appropriate for pulps but less selective than solvent extraction in its reactions with exchange ions⁷⁵. The method is less easily adapted to continuous operation (for large scale applications) than solvent extraction, but can deal with both dilute and concentrated liquors⁷⁵. This topic is reviewed in more detail in Chapter 4, but with the uncertainty existing in treating pulps by either method, it was decided rather arbitrarily to base the work on solvent extraction and to use for this purpose reagents of a type already proved industrially for use in the treatment of clear boron liquors. The reagents considered in detail herein are 2-ethyl-1,3-hexane-diol (EHD) and 2-chloro-4-(1,1,3,3-tetramethyl-butyl)-6-methyl-phenol (CTMP).

It has been the objective of the present work to study the behaviour of both "pure" mineral phases from a variety of sources and also for purposes of comparison, an ore and also effluents obtained (for convenience) from the Etibank Kirka Boraks Isletmesi (Kirka Borax Plant - Etibank) Eskisehir/Turkey.

CHAPTER 2

SAMPLING AND MINERAL APPRAISAL

2 SAMPLING AND MINERAL APPRAISAL

Part of the work in this thesis concerns experiments carried out on natural mineral aggregates. In order to ensure adequate precision in such experiments, it is necessary to have regard to the properties of relevant minerals and to collect and appraise samples of them according to carefully controlled procedures. This chapter therefore has three main considerations: the properties of the minerals, sampling, and determination of the characteristics of the mineral phases.

2.1 Boron minerals

More than 200 boron minerals have been identified but only a few of them are of major commercial importance². An abridged list showing the more abundant members is given in Table 2.1 for reference and some seventeen of these are considered again in Table 2.2 together with some of their definitive properties compiled from Dana⁷⁶ and Read⁷⁷. Figure 2.1 shows the phase composition relationships between the different 'oxides' making up the members (once again for reference). As can be seen, boron minerals have a fundamental similarity to each other and in general form mechanically soft, complex, structures having a low density and relatively high solubility in aqueous media. The position of boron near the beginning of the periodic table ensures that its compounds contain anionic boron covalently bound in a wide variety of complex crystal structures, often containing polymeric species (based on tetrahedral and/or trigonal planar units), and belonging to almost any

TABLE 2.1. BORON MINERALS

Name	Chemical Formula	B ₂ O ₃ / %
Paternoite	MgB ₈ O ₁₃ ·4H ₂ O	71.26
Boracite	Mg ₅ B ₁₄ O ₂₆ ·MgCl ₂	62.31
Ezcurite	Na ₄ B ₁₀ O ₁₇ ·7H ₂ O	61.92
Sassolite	H ₃ BO ₃	56.31
Tunnelite	SrB ₆ O ₁₀ ·4H ₂ O	53.70
Colemanite	Ca ₂ B ₆ O ₁₁ ·5H ₂ O	51.00
Kernite (Rasorite)	Na ₂ B ₄ O ₇ ·4H ₂ O	50.96
Hydroboracite	CaMgB ₆ O ₁₁ ·6H ₂ O	50.53
Priceite (Pandermitte)	Ca ₄ B ₁₀ O ₁₉ ·7H ₂ O	49.84
Probertite (Kramerite)	NaCaB ₅ O ₉ ·5H ₂ O	49.56
Meyerhofferite	Ca ₂ B ₆ O ₁₁ ·7H ₂ O	46.72
Ulexite	NaCaB ₅ O ₉ ·8H ₂ O	46.30
Pinnoite	MgB ₂ O ₄ ·3H ₂ O	42.47
Inderborite	CaMgB ₆ O ₁₁ ·11H ₂ O	41.50
Szaibelyite	Mg(BO ₂) (OH)	41.38
Inyoite	Ca ₂ B ₆ O ₁₁ ·13H ₂ O	37.78
Inderite (Kurnakovite)	Mg ₂ B ₆ O ₁₁ ·15H ₂ O	37.55
Tincalconite	Na ₂ B ₄ O ₇ ·5H ₂ O	47.80
Borax (tincal)	Na ₂ B ₄ O ₇ ·10H ₂ O	36.10
Howlite	Ca ₄ Si ₂ B ₁₀ O ₂₃ ·5H ₂ O	44.47
Veatchite	SrB ₆ O ₁₀ ·2H ₂ O	59.93
Frolovite	Ca ₂ B ₄ O ₈ ·7H ₂ O	38.52
Kahborite (Hemztite)	KMg ₃ B ₁₁ O ₂₀ ·9H ₂ O	49.49
Larderellite	(NH ₄) ₂ B ₁₀ O ₁₆ ·4H ₂ O	72.50
Nobleite	CaB ₆ O ₁₀ ·4H ₂ O	61.98
Gowerite	CaB ₆ O ₁₀ ·5H ₂ O	58.84
Lunenburgite	Mg ₃ B ₂ (OH) ₆ (PO ₄) ₂ ·6H ₂ O	-
Datolite	2CaO·H ₂ O·B ₂ O ₃ ·2SiO ₂	21.75
Turmaline	Al, Mg, Fe ²⁺ , Mn, Ca, Na, K, Li, H, F, B, Si, O -	-
Bandylite	CuB ₂ O ₄ ·CuCl ₂ ·4H ₂ O	19.88
Teepleite	Na ₂ B ₂ O ₄ ·2NaCl·4H ₂ O	21.72
Hambergite	Be ₂ (BO ₃)(OH)	-
Axinite	(Ca, Fe ²⁺) ₃ Al ₂ BO ₃ / Si ₄ O ₁₂ / OH	-

TABLE 2.2. PROPERTIES OF SOME BORATE MINERALS

Name	Crystal System	Optical Sign	Refractive indices nx ny nz	2V	hardness	Sp. gravity
Sassolite	Tr	-	-	-	1	1.48
Borax	M	B(-)	1.4466, 1.4687, 1.4717	39°58'	1.7	2-2.5
Kernite	M	B(-)	1.454, 1.472, 1.488	80°	1.95	3
Colemanite	M	B(+)	1.5863, 1.5920, 1.6140	55°	2.42	4-4.5
Ulexite	Tr	B(+)	1.491, 1.504, 1.520	73° ⁺ 1°	1.9	1
Boracite	C, T	B(+)	1.6622, 1.6670, 1.6730	82½°	2.95	7
Priceite	Tr	B(-)	1.572, 1.591, 1.594	42°56'	2.42	3-3.5
Probertite	M	B(+)	1.514, 1.524, 1.543	73°	2.14	3.5
Tincalconite	H, R	U(+)	1.461, - 1.474	-	1.89	-
Hydroboracite	M	B(+)	1.520, 1.534, 1.569	60°-66°	2.167	3
Inderborite	M	B(-)	1.483, 1.512, 1.530	80°-86°	2.00	3.5
Meyerhofferite	Tr	B(-)	1.500 1.535, 1.560	78°	2.12	2
Inyoite	M	B(-)	1.495, 1.51, 1.520	70°	1.875	2
Kurnakovite	M	B(-)	1.489, 1.510, 1.525	80°	1.85	3
Inderite	Tr	B(-)	1.488, 1.508, 1.515	63° ⁺ 3°	1.86	3
Howlite	M	B(-)	1.586, 1.598, 1.605	large	2.53-2.59	3.5
Tunnelite	M	-	1.519, 1.534, 1.569	-	2.40	2.5

Abbreviations

Monoclinic:	M	Rhombohedral:	R
Triclinic:	Tr	Tetrahedral:	T
Hexagonal:	H	Biaxial:	B
Cubic	C	Uniaxial:	U

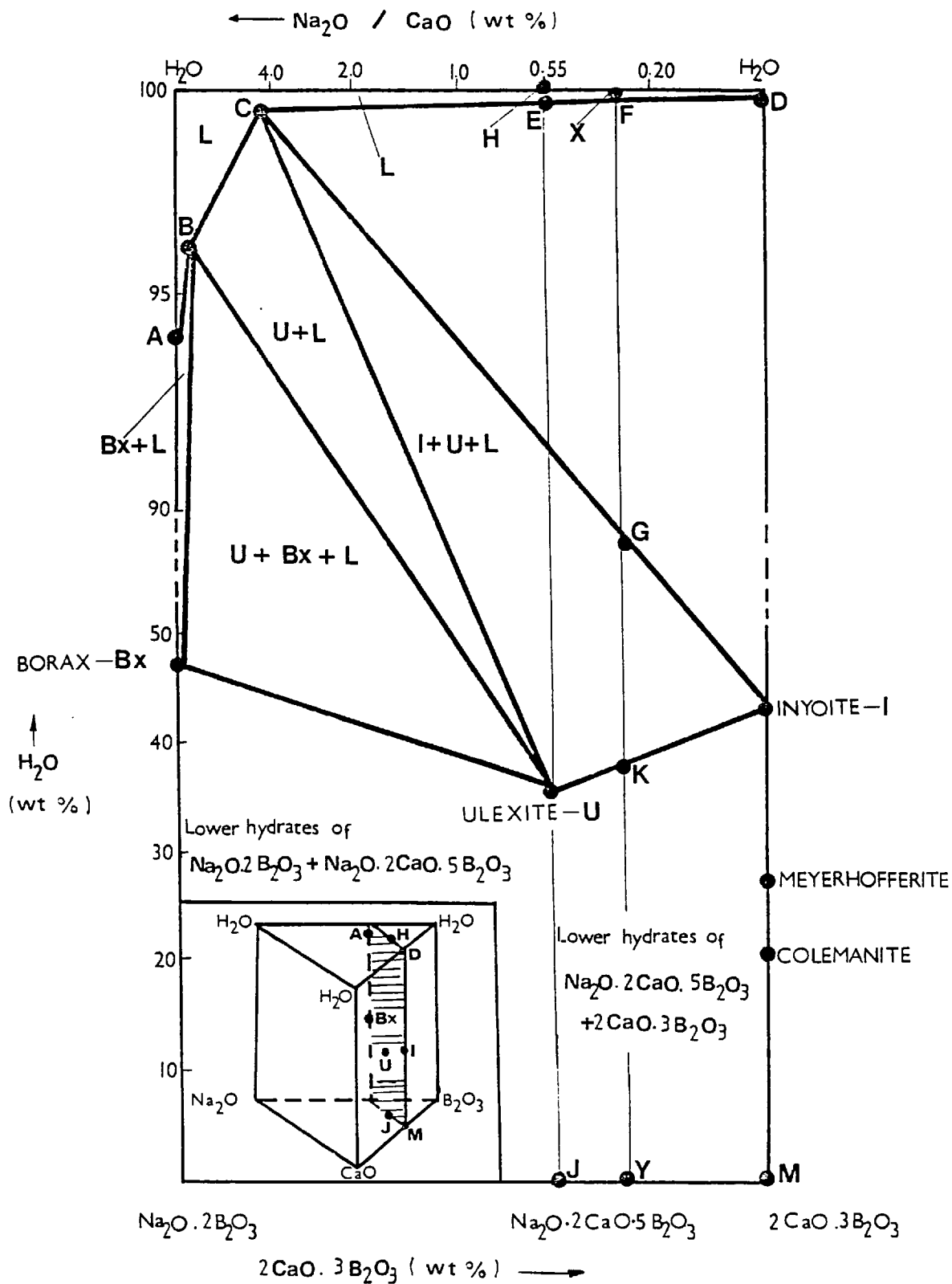


Fig. 1.1. Semi-quantitative phase diagram for the system
 $\text{Na}_2\text{O}-\text{CaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$

one of the seven crystal systems. A typical example is the monoclinic structure given by Wells⁷⁸ for potassium pentaborate tetrahydrate ($\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$) which is illustrated in Fig. 2.2.

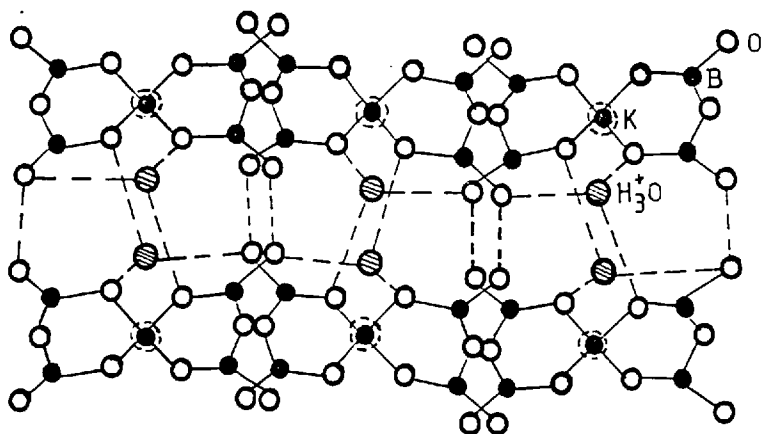


Fig. 2.2. Projection of the structure of Potassium pentaborate tetrahydrate⁷⁸ $[\text{KH}_2(\text{H}_3\text{O})_2 \text{B}_5\text{O}_{10}]$.

The abundant members in Table 2.2 are all minerals of Na, Ca, and/or Mg and often exist as well-formed phenocrysts of a glassy-white appearance showing clearly developed anisotropic features. The

calcium members are seen to be generally harder and less soluble than the others and they also tend to have higher refractive indices. Despite these differences, however, unambiguous identification is rarely straightforward because of the lability of different phases and their general similarity. Thus, a wide range of techniques is necessary to accumulate complementary data for mineralogical appraisal. These include elemental assay (see also Chapter 3), general appearance, petrological microscopy, Geoscan, X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTA) and solubility.

With regard to general appearance, several minerals are illustrated in Fig. 2.3. While these are museum specimens they are

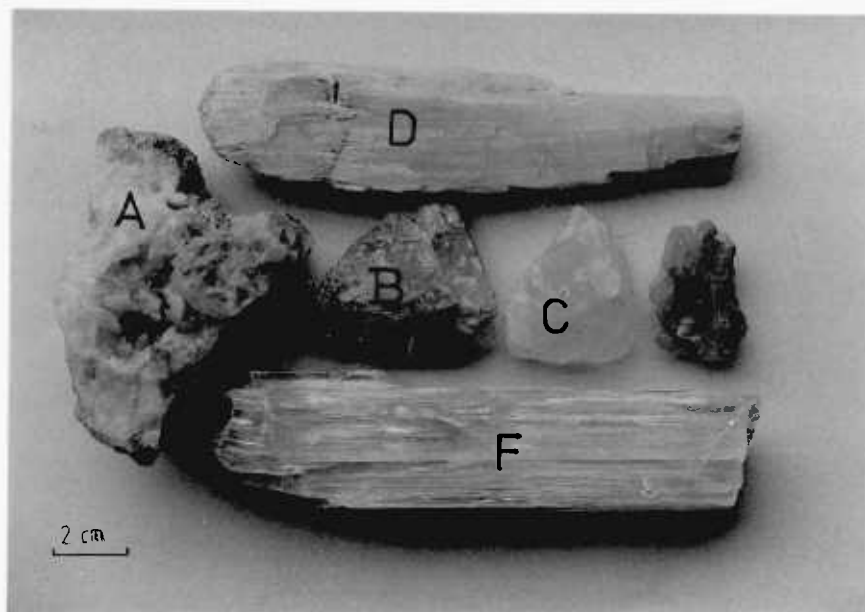
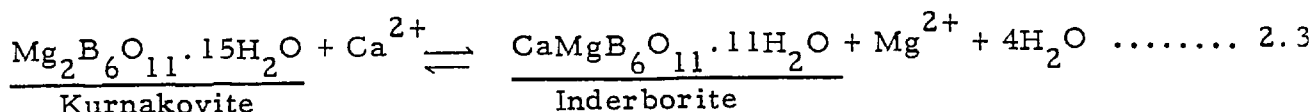
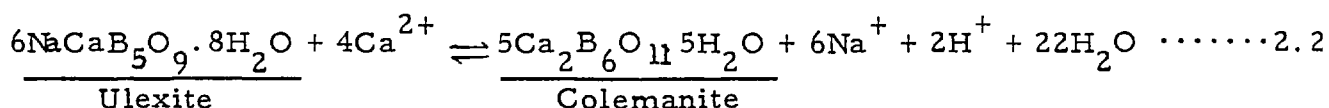
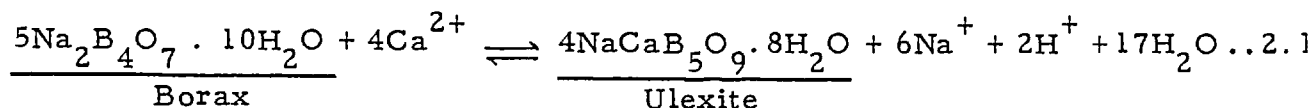


Fig. 2.3. Boron minerals: (A) Colemanite, (B) Kurnakovite, (C) Borax, (D) Ulexite, (E) Tunnelite, (F) Kernite.

not essentially atypical of the well-formed crystals which result from geochemical crystallisation. Borax is prismatic and readily effloresces in air with the formation of a white powdery layer of tincalconite; ulexite is needle-like, and colemanite has a characteristic "cauliflower" structure. Figure 2.4 shows typical diagrams representing XRD⁷⁹, DTA⁷⁹, and solubility data⁴ for some boron minerals.

The first two of these can be used for identification and fingerprinting, while the latter gives information on the relative solubility of phases at various temperatures and has a bearing on the formation of secondary from primary minerals in nature (equations 2.1 - 2.3).



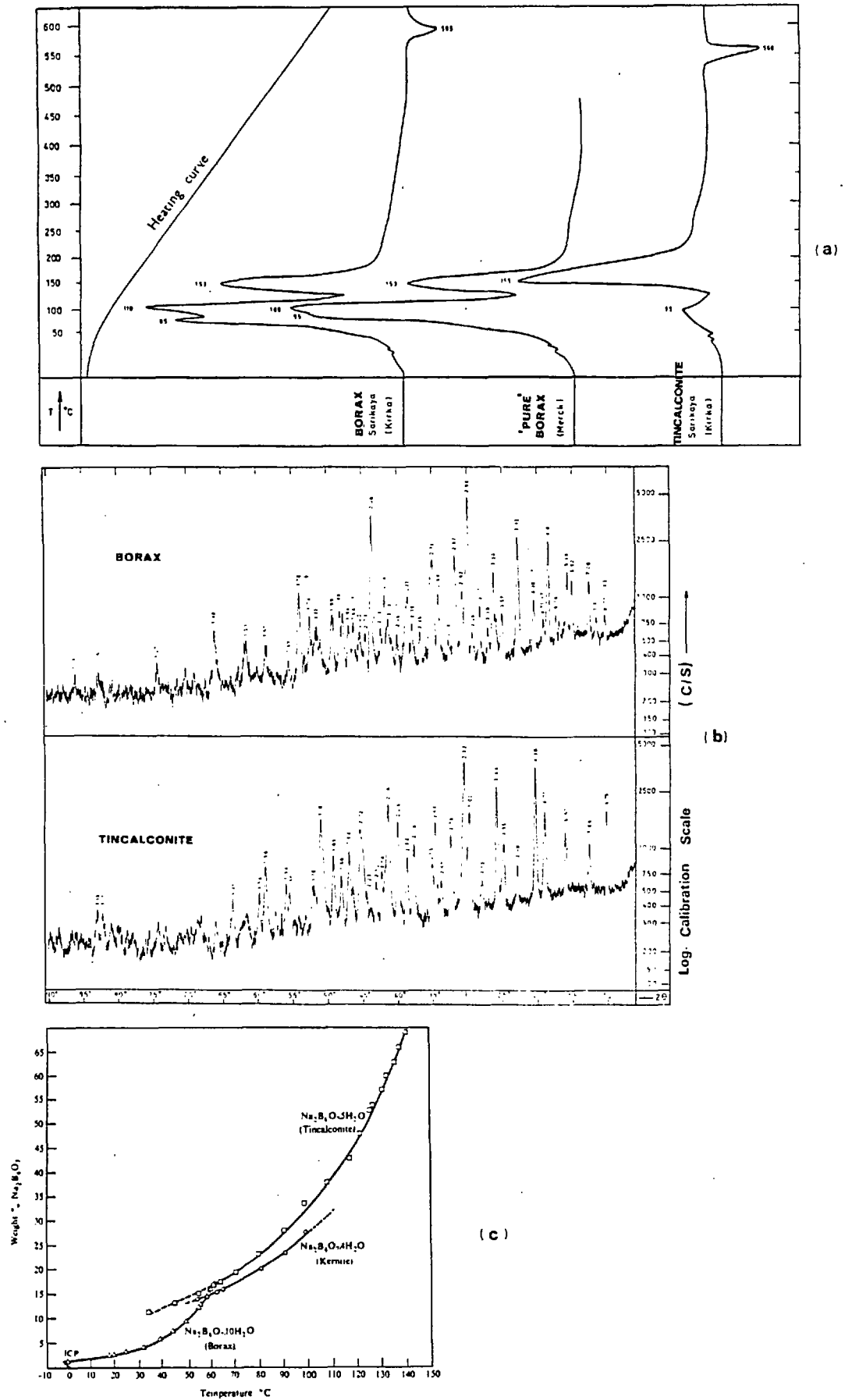


Fig. 2.4. Typical diagrams representing DTA(a), XRD(b) and solubility data (c) for some boron minerals.

2.2 Sampling and assay

2.2.1 Head sampling

While the composition of feed to a typical industrial processing plant must be expected to vary somewhat from day to day, it is valuable to ensure as far as possible that mineral samples taken from that plant are representative. For this purpose, it is necessary firstly to understand the full flowsheet so that sampling can be undertaken at the most appropriate points, and secondly, to take the samples in an acceptably precise manner.

The operation at Kirka (Figs. 1.9 and 2.5), which provided



Fig. 2.5. Photographs of the Kirka operation: (1) the washery showing the spirals, hydrocyclones and scrubbers; (2) the open pit showing 3 m benches.

samples (in 1976) for the present work, has been outlined in Chapter 1. In more detail, crude ore from the open pit is reduced to -25 mm. in a series of crushing, screening and conveying operations involving impact and (closed circuit) hammer mills. The resulting material is further crushed in closed circuit to -6 mm by means of rolls, and scrubbed with saturated borax solution to remove clays in a series of six rotating disc scrubbers. The scrubbed material is screened at 1 mm using fresh water sprays with the oversize going directly to Racklet continuous centrifuges and the undersize being deslimed in cyclones and spiral classifiers, the coarser split joining the main stream to the centrifuges. The cyclone and classifier overflows are pumped to two thickeners operating with superfloc 215 as flocculant. The thickener overflow is recycled to the plant for scrubbing operations and the underflow containing only 4-5% solids goes to the tailings pond. The latter has a total capacity of $4 \times 10^6 \text{ m}^3$ and receives roughly 10^3 m^3 of effluent per day. As the major constituents other than water are montmorillinite-type clays, the subsequent settling rate is very slow and gives rise to the potential pollution problem mentioned previously.

For the present work, samples were taken from the short conveyor (Fig. 1.9) immediately after the grizzly and also from the pulp outflowing from the thickeners underflow discharge pump box. The purpose was to obtain reasonably representative samples of the ore and of the tailings effluent. In the first case, it was concluded that a truly representative sample could not be taken because of the great difference in particle size between the major borax and clay constituents, bearing

in mind that the product samples had to be restricted in bulk for shipping. Approximate calculations using Gy's formula⁸⁰ showed that 5-10 tonne of sample should have been taken to avoid significant errors in sampling - this despite the helpful routine practice undertaken by the company of blending the ore before it reaches the crushing section. The alternative of sampling further along the line was difficult because even the simple process of screening leads to partial separation of the mineral phases for such soft and variable materials. A compromise was used in which -20 cm chunks of ore were selected from the conveyor belt to give a total sample over several days of 176 kg.

In the second case (tailings) such problems did not arise owing to the much smaller average particle size, although it was necessary to ensure a fully mixed product. Suitable conditions were found in the vigorously agitated pulp (plant-end slurry) emerging from the thickeners. It was found to be difficult if not impossible to sample the tailings pond directly because of restricted access and inefficient settling. Results for these sampling operations are given below.

Experimental

The coarse sampling was achieved by selecting specimens by hand at short time intervals for several shifts. In order to prevent any decrepitation the bulked samples were carefully sealed at the earliest opportunity. For the slurry sampling a standard device⁸¹ was constructed and filled by rapid insertion into the slurry so as to cut the whole stream momentarily. In these operations only one sample of about 500 cm³ was taken per shift for 10 days and the samples bulked together and

sealed. No attempt was made to assess the precision of these sampling operations. Table 2.3 shows some of the data obtained, and these will be discussed later.

TABLE 2.3. ANALYSIS OF SAMPLES FROM THE KIRKA OPERATION

Sample (day) No.	Feed/%B ₂ O ₃	Concentrate/%B ₂ O ₃	Tailing/%B ₂ O ₃
1	20.8	29.2	1.89
2	25.6	33.1	1.41
3	24.4	31.2	1.21
4	26.6	32.7	1.91
5	27.2	32.0	1.97
6	25.4	33.2	1.57
7	24.6	33.4	1.65
8	24.5	31.9	1.45
9	25.3	32.6	1.93
10	26.6	32.9	1.84
Mean	25.1	32.2	1.68
Standard deviation(σ)	1.70	1.20	0.26
Variance (σ^2)	2.89	1.43	0.07
Error/%	7	4	15
Average concentration factor: 1.28			
Average recovery/% (for 100 tonne per hour of feed and 67 tonne of concentrate) : 86			

2.2.2 Sub-sampling and sample preparation

Although the head sample is unlikely to be closely representative of plant feed over an extended period it may be assumed to be sufficiently so for present purposes. Sub-sampling can be made with much improved precision. Figure 2.6 shows the scheme used together with the minimum fundamental errors likely to be incurred, calculated according to the revised method of Gy⁸⁰.

The scheme was devised to keep the random errors of sampling within about 3% and assumed that systematic errors would be smaller than this. No purpose would seem to be achieved by working to a closer tolerance. According to Gy⁸⁰ the relative variance of fundamental error (σ_{FE}^2) of sampling of broken ores for assay is given by:

$$\sigma_{FE}^2 = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) m.l.f.g.d^3 \dots \dots \dots 2.4$$

where M_S and M_L are the weights (g) of the sample and total population respectively; m is the mineralogical index ($g\ cm^{-3}$) expresses as:

$$m = \frac{(1 - a_L)^2}{a_L} \rho_V + (1 - a_L) \rho_G$$

and for which a_L is the mineral content as (a fraction) of the population ρ_V is the density ($g\ cm^{-3}$) of the valuable mineral and ρ_G the corresponding density of the gangue; l is the liberation factor which takes a value between 0 and 1 in accordance with the tabulation

d/d_0	<1	1-4	4-10	10-40	40-100	100-400	> 400
1	1	0.8	0.4	0.2	0.1	0.05	0.02

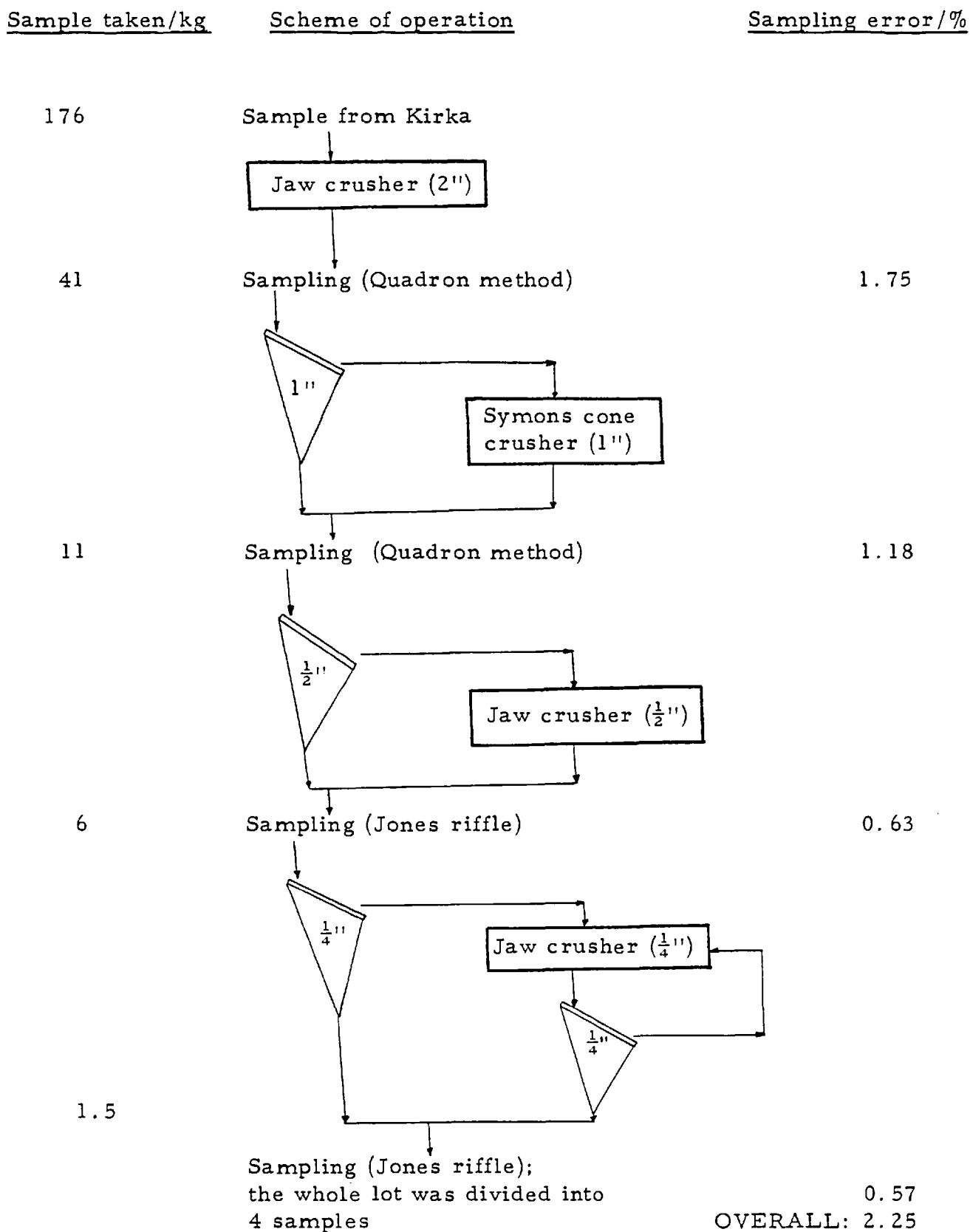


Fig. 2.6. Sampling scheme used in preparing the sample from Kirka operation

d being the actual size (cm) of the largest particles (strictly, that screen size retaining 5% by weight of the sample) and d_0 the estimated liberation size; f is the shape factor which for all common ores takes a value of 0.5; and g is the size distribution factor commonly taken to be 0.25.

The results of calculations using equation 2.4 are commonly expressed in terms of percent error which is the same as relative error (%). Thus,

$$\sigma^2 = \left(\frac{a \Delta a}{200} \right)^2 \dots \dots \dots 2.5$$

where σ is the standard deviation, σ^2 is the variance, a is the grade (%) of valuable mineral and Δa is the relative error (%) of a% at the 95% confidence limit; and

$$\sigma_{FE}^2 = \left(\frac{\sigma}{a} \right)^2 \dots \dots \dots 2.6$$

from which the desired quantities may be calculated.

The normal practice of obtaining samples for assay and mineral appraisal involves a number of stages of communiton and sampling. Each sampling stage will have its own associated errors which must be correctly summed to give an estimate of the overall error. For this purpose, the additive property of variance⁸² is used and the total relative error deduced.

Experimental

All operations were carried out as quickly as possible - within two days - to avoid unnecessary dehydration of the minerals. The ore (176 kg) was first crushed to -2" by means of a 12" Blake Jaw crusher and the resulting mixture coned and quartered according to

standard practice⁸³. A quarter (44 kg) of the product was crushed to -1" (with intermediate screening) by means of a standard Symons cone crusher and similarly coned and quartered to give an 11 kg sample. The latter was further crushed in two stages in a small 6" Blake Jaw crusher, firstly with a jaw setting of $\frac{1}{2}$ " and secondly with $\frac{1}{4}$ ". The final product was divided into two using a Jones riffle⁸³, and then one of the halves (6 kg) was further split into the working lots A - D referred to in Fig. 2.7.

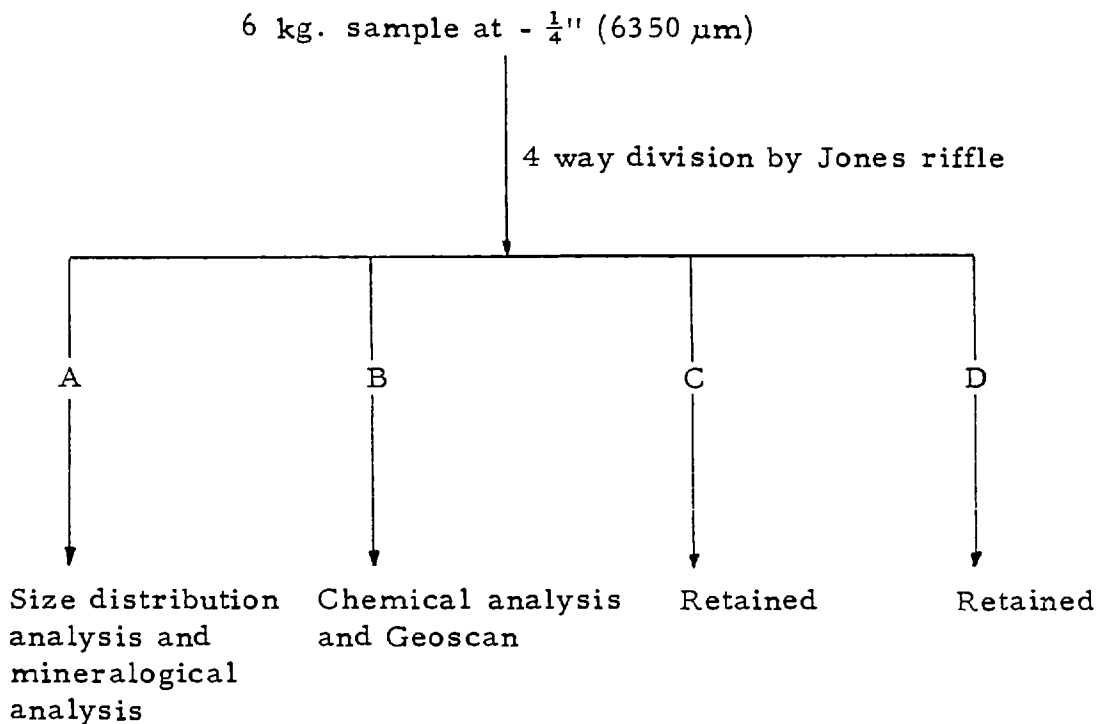


Fig. 2.7 Use of crushed samples.

The estimated overall sampling error at this stage was 2.25%. Particle size distribution, obtained with the aid of stacks of Endecotts (test sieves) screens in the standard manner⁸⁴, are reported in Table 2.4.

TABLE 2.4. SIZE DISTRIBUTIONS

Screen Size (μm)	Sample A			Sample B (after grinding)		
	wt/g	wt/%	Σ wt/%	wt/g	wt/%	Σ wt/%
-6350 +2360	720	53.7	100.0	-	-	-
-2360 +1180	230	17.2	46.3	-	-	-
-1180 +425	211	13.7	29.1	-	-	-
-425 +212	78	5.7	13.4	-	-	-
-212 +150	25	1.9	7.7	-	-	-
-150 +106	24	1.8	5.8	17.8	17.8	100.0
-106 +75	16	1.2	4.0	27.2	27.2	82.2
-75 +53	14	1.0	2.8	23.7	23.7	55.0
-53	24	1.8	1.8	31.3	31.3	31.3
TOTAL	1342	100.0	-	100.0	100.0	-

Sample B was prepared for assay by grinding in a $8\frac{1}{2}$ " diameter disc pulverator, giving a final sample of 10 g of homogeneous material at -150 μm . Further testwork carried out on samples A and B and also on the slurry is described below.

2.2.3 Assay

Chemical assay and X-ray fluorescence (XRF) analysis were undertaken by Analytical Services (Imperial College) on three samples: (1) that taken from sample B (Fig. 2.7) - E_1 , (2) a sample taken from the slurry and centrifuged and dried - K_1 (see section 2.3.2),

(3) a sample taken from the slurry (see section 2.3.2), evaporated and dried - K_2 . The results are given in Tables 2.5 and 2.6 and discussed later.

TABLE 2.5. RESULTS OF CHEMICAL ANALYSIS

Constituents	F_1 Ore sample/%	K_2 Slurry sample evaporated/%	K_1 Slurry sample Centrifuged/%
SiO_2	2.33	18.98	12.65
Al_2O_3	0.53	2.89	1.65
Fe_2O_3	0.14	0.53	0.35
TiO_2	0.02	0.08	0.06
CaO	3.35	16.40	11.05
MgO	2.33	15.25	14.20
SrO	0.40	1.10	0.70
$Na_2O(Na)$	12.36	1.50*	10.73
$K_2O(K)$	0.52*	1.35*	1.20*
$Li_2O (Li)$	0.038*	0.160*	0.120*
B_2O_3	33.43	19.12	8.20
CO_2	3.94	22.05	15.65
H_2O	30.56	4.12	8.63
TOTAL	94.39	104.5	89.31
(* Flame emission)			

TABLE 2.6. RESULTS OF X-RAY FLUORESCENCE (XRF)

Sample	Inter	Minor	Trace	Major
F ₁	Na	Mg, Al, Ca	Cl, K, Ti, Fe, Sr, Cs	-
K ₂	Ca	Mg, Al, Si, K, Fe, Sr	Ti, Mn, Cs	-
K ₁	Ca	Mg, Al, Si, Fe, Sr, K	Ti, Cs, K	-
(%)	5-0.5	0.5 - 0.05	< 0.05	>5

Note: While dissolving the samples, it was found that F₁ was highly carbonated, K₂ was next in order and K₁ was least.

2.3 Mineralogical appraisal

Examination of hand specimens from the sample taken from Kirka-Eskisehir show that boron mineral crystals up to 2 cm. in size are present. The appearance varies from glassy-colourless to greyish-white. The ore is in the form of compact aggregates of clay and boron minerals as breccia and layers. The gangue matrix consists mostly of clay minerals but some carbonates are also present. As expected dehydration occurred in the atmosphere and it was observed that clear glassy crystals became opaque within 2 - 3 days under these conditions, with the formation of tincalconite.

Typical hand specimens consisted of almost monomineralic borax zoned and interlayered with clays and invariably subject to partial alteration to tincalconite on exposed surfaces.

Detailed studies centred on optical microscopy of thin sections and on examination using a Geoscan electron probe micro-analyses of suspensions of crushed material cemented in araldite.

2.3.1 Thin sections

Thin sections were prepared from several selected hand specimens. This presented problems owing to the solubility of the minerals in water and in organic solvents, but the use of borax-saturated water resolved this difficulty.

Experimental

The main criteria employed were refractive index (n), interference figures ($^+$) and the angle between the two optical axes in biaxial minerals ($2V$).

Thin sections were prepared by cutting a rock specimen with the aid of a 'Cutrock' diamond wheel, grinding on a similar wheel to about $\frac{1}{8}$ " thickness, polishing on one side successively with carborandum (220C - 600C), 3-6 μm diamond paste, and 1 μm diamond paste on 'Struers' wheels and then Aralditing this side to a glass slide. The other side was treated similarly until the thickness was 30 μm and finally this second side was sealed with 'Trycolac' liquid cover glass.

Microscopic examination (Vickers Polarising Microscope) of the sections at 100X and 400X showed the gross mineralogical features to be consistent with those observed in the original hand specimens. The determinative method was as follows:

(1) The slide was placed under the microscope and a comparative estimate was made of refractive indices of adjacent phases by means of the movement of the Beckeline⁸⁵.

(2) The optical sign of the selected mineral phases was measured with the aid of an accessory quartz wedge, under crossed nicols.

(3) The angles between crystallographic axes (2V) were estimated for the biaxial members (all phases considered to be biaxial with the exception of tincalconite), by viewing the shapes of the isogyres appearing under crossed nicols. Values were classified as low (up to 40°) moderate (40-70°) and high (70-90°).

Combined application of 1 - 3 above permitted positive identification of borax, colemanite, tincalconite, ulexite, kurnakovite, kernite, inyoite and tunnelite.

It was apparent from examination of both slides and hand specimens that although many grains were almost pure borax, there were regions in which the mineral was fine grained and interlayered with clay minerals. In these, fine inclusions of unidentified matter caused colour changes to light-pink, yellow and grey. Tincalconite and kernite appeared to be exclusively the alteration products of decomposition of borax, with kernite being mainly in clay matrices and tincalconite at the boundaries of borax minerals. Ulexite occurred in the shape of white/grey 'cotton balls' (having a silky luster) at the borax-clay boundaries; inyoite was observed as colourless microcrystalline aggregates; colemanite was found interbanded with clay in association with inyoite and ulexite; kurnakovite and tunnelite were observed in the clay matrix as

individual microcrystals; and meyerhofferite appeared to be in close association with other calcium borates.

2.3.2 Geoscan studies

Electron probe X-ray micro-analysis was carried out using a Cambridge Geoscan instrument to estimate semi-quantitatively the relative proportions of minerals present in the samples.

Experimental

Two types of material were considered : (1) sample B (Fig. 2.7) and (2) slurries (section 2.2.1).

(1) 10 g of sample B, after grinding to $-150\ \mu\text{m}$ (section 2.2.2) was cemented in Araldite to form a tablet 1" in diameter and 0.5 cm thick, (containing 15% $0.5\ \mu\text{m}$ graphite to improve the surface conductivity), and polished on both sides in a manner similar to that described in section 2.3.1.

(2) A $50\ \text{cm}^3$ aliquot of slurry was taken from the vigorously mixed bulk sample by means of a wide-ended pipette, and centrifuged to obtain the solid portion. This portion was separated by decantation and rapidly dried at about 40°C . The dry material was cemented in Araldite as above.

The method of obtaining the relative proportions of the minerals was briefly as follows:

(1) The spectrometers were set up to obtain characteristic X-ray signals for the elements Na, Ca, Mg, Si and Sr and standardized

against the purified materials NaCl , CaF_2 , Mg , SiO_2 and Sr .

(2) The surface of the tablet was scanned (52 min) at a constant rate of 1200 μm per min. and at a constant chart speed of 80 mm per min, and two parameters were simultaneously measured for the five elements: the intensity of the X-ray signal (related to the proportion of the five elements in the mineral phase being traversed), and the length of traverse (related to the width of the mineral phase in the surface of the tablet).

(3) The incidence of each mineral phase in the surface of the tablet was deduced from the relative intensities of X-ray signals for the different elements and their theoretical proportions in the various boron minerals of interest. Thus for ulexite relevant percentages are 5.67% Na and 9.98% Ca and the mineral is expected to give X-ray signal intensities in this ratio after correction according to the standards.

(4) The relative proportions of each mineral were deduced by summing the individual distances traversed and working out the ratio (for mineral A):

$$\%A = 100 \quad L_A / L_T \quad 2.7$$

where L_A is the length traversed (μm) for a particular mineral phase and L_T is the corresponding total length traversed.

The results obtained are given in Table 2.7 and are discussed in section 2.4.

TABLE 2.7. MINERALS AND THEIR PROPORTIONS IN SAMPLES FROM KIRKA

Minerals	Chemical Formula	Ore sample Prop. /%	Slurry sample Prop. /%
Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	15.7	-
Ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$	12.4	0.5
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$	3.5	0.8
Kernite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	8.1	-
Tincalconite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	9.1	-
Inderborite	$\text{CaMgB}_6\text{O}_{11} \cdot 11\text{H}_2\text{O}$	10.5	1.8
Hydroboracite	$\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$	1.9	0.1
Inyoite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$	5.8	1.2
Kurnakovite (Inderite)	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$	2.0	0.3
Meyerhofferite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$	1.3	0.2
Tunnelite	$\text{SrB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$	6.0	0.9
Clay minerals	(montmorillonite, hectorite, illite)	11.5	52.3
Calcite	CaCO_3	3.4	14.1
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	4.7	18.2
Unknowns		4.1	9.2
TOTAL		100.0	100.0

2.4 Discussion

If a new unit operation such as solvent extraction is to be proposed for integration into a complex circuit, it is important to assess not only the composition of the feed and effluent from that operation but also the overall composition of the ore and how this changes during the treatment steps⁸⁶. It was therefore considered necessary to study the ore itself in detail even though the main experimental investigations primarily concerned the effluent slurries. The work in this chapter has been aimed therefore at accumulating sufficient basic data on both the ore and the slurries to facilitate solvent extraction studies and viable recommendations for changes in existing plant flowsheets.

The problem of representative sampling of primary raw materials is normally severe⁸⁰ because of large systematic and random errors likely to be introduced in handling particles which are grossly heterogeneous with respect both to size and mineralogical composition. In the foregoing sections it was shown that a closely representative sample of the Kirka ore could not be taken (although the slurries presented a much smaller problem). It was nonetheless considered important to treat the head sample as representative and to sub-sample this with good precision, if for no other reason, because this was the only procedure which would permit consistent results to be obtained in subsequent experimental work. A large quantity of this head sample (> 100 kg) remains available for further work, and providing this is itself carefully sampled, results should be directly comparable with those given in later chapters of this thesis.

Table 2.3 represents routine acid/base titrimetric assays of plant feed and products taken on the days that the sampling was undertaken. As can be seen, there are considerable day to day variations in feed grade and this is reflected in the composition of both the concentrate and tailings. It seems reasonable to assume that the effluent will contain about 1-2% B_2O_3 . The proportion of clays present was not measured day by day. The average concentration factor is 1.28, and assuming a permissible tolerance of 5 ppm B the effluent concentration (as water soluble boron) is about 1000 times that which is environmentally non-destructive. It is evident that production shortfall due to boron losses to the tailings is negligible, but that a potential pollutant is being produced on a large scale.

Sub-sampling and sample preparation were carried out according to established practice⁸³ and an acceptable random error was achieved (2.25%). It was not feasible to take close account of biases, particularly those automatically incurred through mechanochemical dehydration⁸⁷, and these had to be assumed to be small. As shown in Fig. 2.6, errors decreased with decrease in particle size and gave a total of 2.25%. This is slightly above the norm but in view of the aforementioned constraints it was not considered worth working to closer tolerances. Table 2.4 shows the degree of success achieved in avoiding production of fines by means of intermediate screening. Thus, for sample A, less than 8% of the material (nominally $-\frac{1}{4}$ " ; 6350 μm) was at $-72 \#$; 212 μm .

Assays obtained are given in Table 2.5. The boron content

of the ore is higher than that obtained at the plant (Table 2.3); no clear reason can be given for this difference, except to state that boron determination is particularly susceptible to systematic error (see Chapter 3). The main difference evident between the ore and the treated slurries are those expected: gangue constituents containing Si, Ca, Mg and carbonate increase while Na and B decrease markedly.

The similarity in the major boron minerals with respect to transmittance of light and other properties makes a study of thin sections by transmitted light more rewarding than a corresponding study of individual grains under the binocular microscope. The latter method was attempted with the aid of the determinative scheme of Jones and Fleming⁸⁸ but was relatively unhelpful. Thus, density, solubility and general appearance were not generally sufficiently distinctive to give a useful modal analysis. However, the refractive index of several individual borax grains was measured and found to compare closely with that given in Table 2.1. Conversely the careful comparison of refractive indices, optical sign and 2V values permitted positive identification of mineral phases in thin sections and this method was therefore used extensively.

Quantitative measurement of the relative proportions of minerals was carried out by Geoscan rather than by grain counting for similar reasons. A highly precise measurement was neither possible nor necessary: in the first instance, it takes at least a week's work to obtain results for scanning a single surface, and many surfaces would need to be scanned to achieve results representative of the bulk⁸⁹;

and in the second instance the inherent variability of the materials reduces the value of high precision. The results obtained are shown in Table 2.7, wherein the main divisions are into boron minerals (76%), clays (12%) and carbonates (8%). for the ore, and similarly 6%, 52% and 32% for the dried slurry. The values are broadly consistent with the chemical assays above and give the further information that although borax is the major constituent the other boron minerals are present in significant amounts together with clays and carbonates. It was not feasible to distinguish individual clays by this method and, indeed, these were only assumed present on the basis of silica content. However, XRD scans on the same materials carried out (on Philips PW 1050/25 wide range goniometer in conjunction with a PW 1310 generator fitted with a copper target and PW 1352 counter and scaler instrument) by R. Shaw indicated clearly the presence of smectite-like clays $d(001): 12-15(\text{\AA})$, $d(060): 1.49-1.54(\text{\AA})$ although even by this method unambiguous identification and measurement was not feasible. It should be noted that the proportion of boron minerals shown in the slurry column (Table 2.7) relates to 'insoluble' phases as the soluble minerals were removed with the liquid phase during centrifuging.

Observation of the Kirka plant (and others in Turkey) soon indicates that the main difficulty lies in effective thickening or settling of tailings. At Kirka the thickeners have difficulty in coping with the throughput without the use of a large dosage of flocculant. This has two major consequences: (1) much needed clear water is not available for recycling to the plant, and (2) the cloudy effluent is lost to the environment with its soluble and solid boron content. The need either for

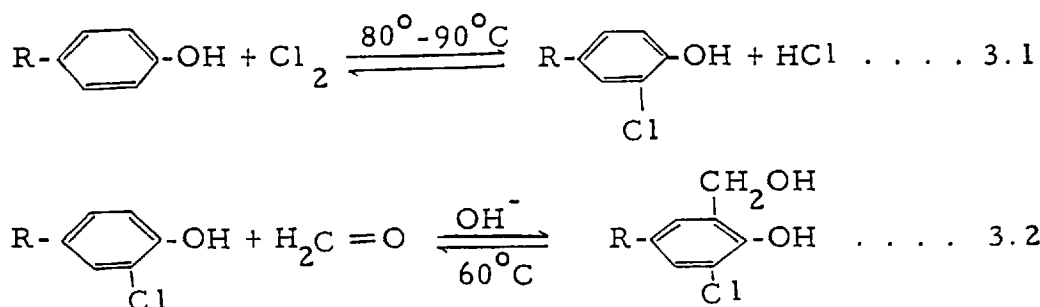
improved solid-liquid separation or for a means of removing the boron content by solvent extraction or ion-exchange is evident.

CHAPTER 3
REAGENTS AND ANALYTICAL TECHNIQUES

There are two main considerations in this chapter: the synthesis and purification of the solvent - 2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylolphenol - which is not commercially available; and the development of reliable analytical techniques for the routine determination of relevant compounds in mixtures resulting from solvent extraction experiments.

3.1 Preparation and purification of 2-chloro-4-(1,1,3,3,-tetramethylbutyl)-6-methylolphenol (CTMP)

It has been reported that 1,2 and 1,3 diols are the most effective groups of extractants for boron values^{68,90,91}. These are highly selective for boron species and readily extract them into the organic phase. Three compounds of this type were selected for the present work (Chapters 4 and 5): 2-ethyl-1,3-hexanediol (EHD), 4-tert-butyl-catechol (TBC) and 2-chloro-4-(1,1,3,3,-tetramethylbutyl)-6-methylolphenol (CTMP). The first two are readily commercially available and they were purchased and used without further purification. CTMP had to be synthesised and this was achieved by the method below which has been developed as a modification of published work^{68,92}. The reagent can be prepared by firstly chlorinating 4-(1,1,3,3,-tetramethylbutyl)-phenol and secondly methylating the product:



In these equations R refers to the group iso-C₈H₁₇.

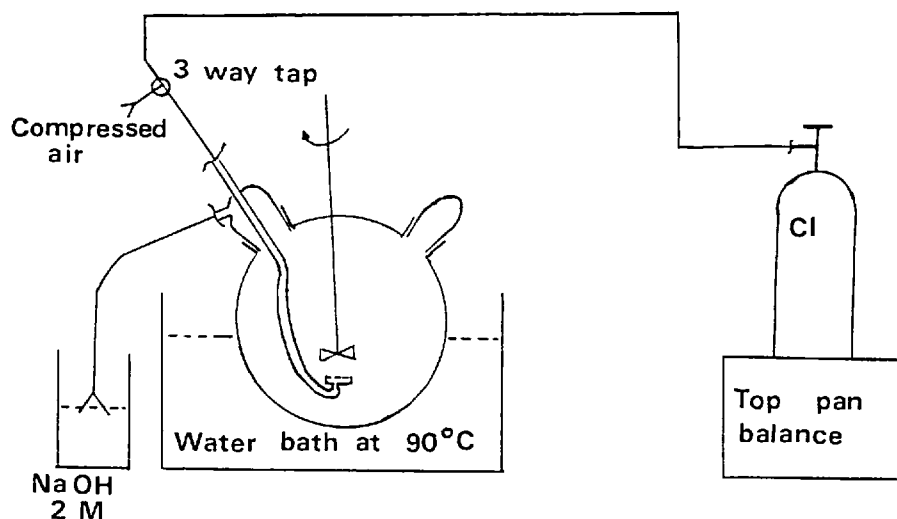
Experimental

Figure 3.1 shows the main features of the apparatus used in chlorination and methylation.

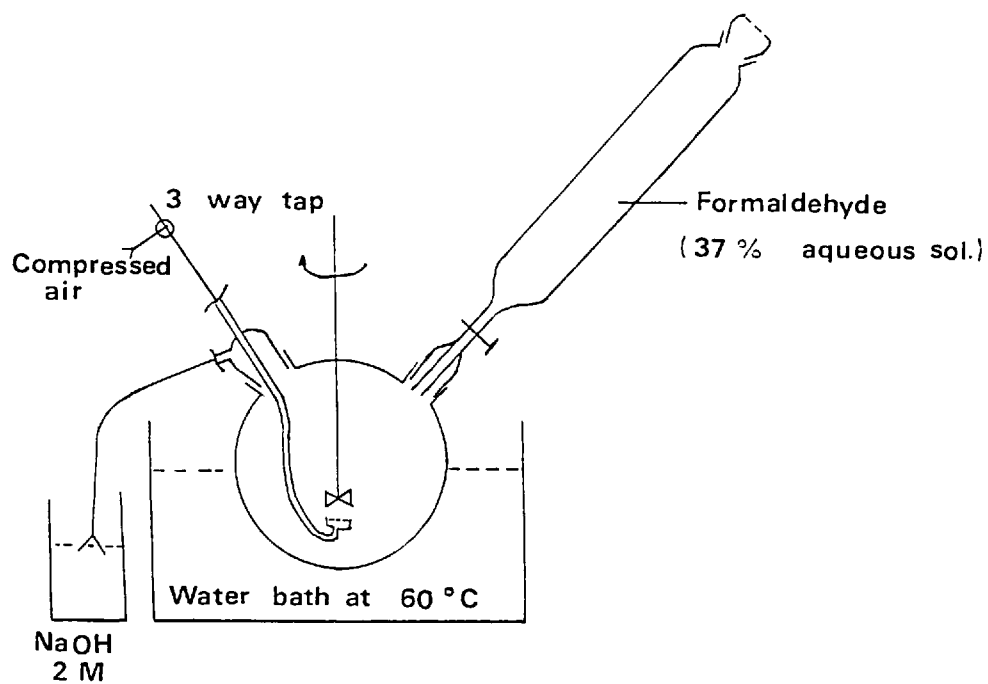
Chlorination: 618.0 g (3 mol) iso-octyl-phenol (Fluorochem Ltd, Derbyshire) were placed in the 1 dm³ three-necked flask shown and heated to 80°-90°C to cause the substance to melt. About 220 g (6.2 mol) chlorine was introduced over a period of 6 hours (at 80-90°C) to the stirred melt from a cylinder (BDH Chemicals Ltd.) connected to a tube reaching to the bottom of the flask. Steady evolution of hydrogen chloride occurred and this gas together with unreacted chlorine was trapped in sodium hydroxide solution (Fig. 3.1(a)). After the reaction period the contents of the flask were cooled to 60°C and a slow stream of air was passed for 12 hours with stirring in order to flush out the last traces of the two gases. The yield was 714 g (99% of the theoretical amount).

Distillation: the chlorinated material was vacuum distilled twice according to standard practice⁹³ using a Perkin triangle for collecting fractions and a Genevac rotary piston vacuum pump for reducing the pressure. That fraction (total 648 g, 90% of the theoretical amount) distilling at 140-150°C at 3-5 mm Hg was collected as 2-chloro-4-(1,1,2,3-tetramethylbutyl)-phenol.

Methylation : the twice distilled material (about 620 g) was placed in the water bath at 60°C (Fig. 3.1(b)), and 72 cm³ of 10% NaOH was added



(a) chlorination of iso-octyl-phenol



(b) methylation of chlorinated iso-octyl-phenol

Fig. 3.1 Apparatus for preparation of CTMP.

dropwise to adjust the pH to 9-10 (the pH of the material after distillation was about 4). 270 cm³ (3 mol) formaldehyde (as a 37% solution in water), obtained from BDH (Chemicals) Ltd., (unless otherwise specified all chemicals were obtained from BDH) was introduced dropwise over a period of 2 hours to the well-stirred mixture. A vigorous reaction occurred with evolution of heat. Stirring was then continued for a further 24 hours to complete the reaction. The two phase product was separated in a tap funnel to give 713 g (88% of the theoretical amount) CTMP as a viscous amber liquid. This material showed an alkaline reaction and was washed several times firstly with dilute HCl and secondly with water before used in further experimental work.

Complex formation: about 70 g CTMP was emulsified with 100 cm³ saturated borax with the aid of vigorous stirring and the ultrasonic probe (Soniprobe, Dawe Instrument Ltd.). The emulsion was left to settle overnight before separating the layers, and dissolving the organic phase in acetone⁹². The acetone solution was concentrated and cooled in stages but there was no significant precipitation of a crystalline phase. Other conditions of temperature, reactant ratio, solvent and recrystallisation were employed with similarly negative results.

It was concluded that the crystallisation of boron complexes was not a suitable method for purifying CTMP. Assay results (Department of Chemistry, Imperial College) on two samples of the product from methylation were as shown in Table 3.1. As can be seen from the Table, CTMP appears to be reasonably pure.

TABLE 3. 1 ANALYSIS FOR THE CONSTITUENTS OF THE CTMP PRODUCED

Constituents	Theoretical %	Sample 1 Found/%	Sample 2 Found/%
C	66.53	65.91	65.26
H	8.56	8.58	8.32
O	11.82	—	—
C.I	<u>13.09</u>	10.79	13.12
TOTAL	100.00		

3.2 Analytical techniques

Investigations into the solvent extraction of borates from liquors require facility for reliable determination of borates and a variety of other species separately and in admixture at concentrations down to 1-5 ppm. This section outlines methods used in the present work for borates, metal cations (Na^+ , Ca^{2+} , Mg^{2+} , and K^+), chloride ions, and CTMP.

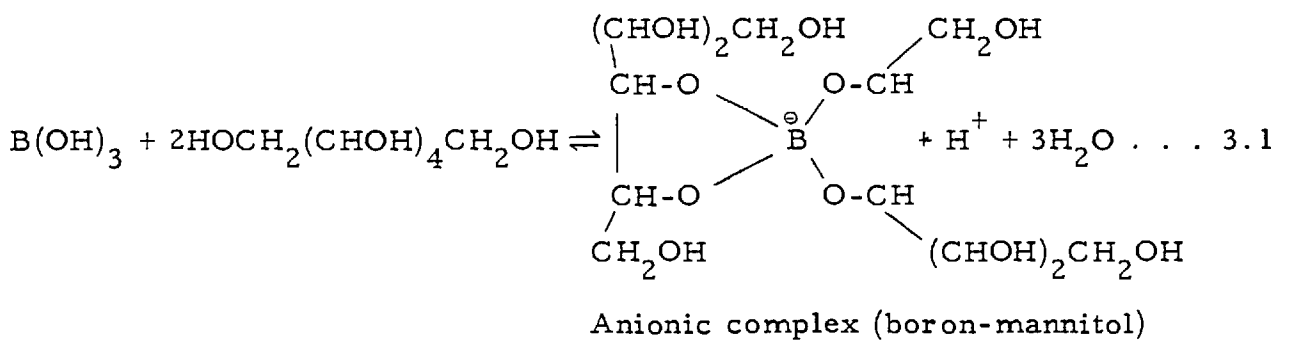
3.2.1 Boron determination

There are three main methods of boron determination in common use: acid/base titration; atomic absorption spectrophotometry (AAS); and colorimetry. Table 3.2 summarises relevant characteristics.

The acid/base method relies on reactions of the type represented in equation 3.1:

TABLE 3.2. ANALYTICAL METHODS FOR BORON

	ACID/BASE	AAS	COLORIMETRY
Min. Conc./ppmB	10-20	10-50	0.01-0.1
Max. Conc./ppmB	Saturated(5000)	1000	1-5
Max. precision/% error	0.2-0.3	3-4	2-4
Time required for a set of 6 samples plus standards/hours	1-2	1-2	6-7
Special reagents	Mannitol, standard acid and alkali	Boron standards	Curcumin, acetic acid, chloroform, sulphuric acid, hydrochloric acid, absolute alcohol.



The acid dissociation constant of boric acid itself is too small in magnitude ($K_a = 6.4 \times 10^{-10}$) to permit direct titration⁹³. Addition of a complexing polyol such as mannitol(powder)increases the acidity sufficiently without otherwise interfering significantly ($K_a = 1 - 2 \times 10^{-4}$ after addition of mannitol).

From equation 3.1 it is clear that $\text{B(OH)}_3 = \text{OH}^-$ in an acid/base titration and therefore $1 \text{ cm}^3 (1\text{M NaOH}) = 0.06184 \text{ g } \text{H}_3\text{BO}_3$.

It is just possible to detect the end point reliably using 0.01 M alkali in conjunction with a pH meter. Assuming a minimum titre of 25 cm³ it is thus possible to deal with solutions down to 20 ppm. The method is quite free from interferences because any free acid or alkali can be neutralised in a preliminary step before adding the mannitol and the subsequent complexing step is near-specific for borates. It is rapid and relatively precise providing care is taken to avoid carbon dioxide absorbtion; and is in routine use in the boron industry⁹⁴.

Atomic absorption determinations are suitable in principle for large numbers of samples requiring results of relatively low precision but otherwise seem to compare unfavourably with the acid/base titration. The AAS method is extensively used in assays of boron in fertilizers⁹⁵⁻¹⁰⁰.

Neither of the above methods can deal with the concentration range 1-10 ppm over which boron pollution becomes significant. There have been many papers on the determination of the element in this range¹⁰¹⁻¹⁰⁹, most of which employ the near specific reaction between circumin $[\text{CH}_3\text{O C}_6\text{H}_3(\text{OH})\text{CH}=\text{CHCO}]_2\text{CH}_2$ and boron species to form intensely violet coloured complexes (similar in nature to that in equation 3.1 but forming a conjugated chain¹⁰¹). The wide differences in detail in these papers suggest that the method is difficult to put into practice and that it requires particularly careful and systematic work together with considerable experience to obtain reproduceable results.

In the present work the acid/base method was used according to established practice⁹³ for the higher concentrations and the colorimetric

method of Goldman et al.¹⁰⁹ using curcumin was adopted in a modified form for the lower end of the concentration range. AAS and other curcumin methods were investigated but were not found to be useful.

Experimental

Acid/base method: Typically, a 25 cm³ aliquot of borate solution was placed in a 250 cm³ beaker and its pH adjusted to 5.4 using standard solutions of 0.05 M NaOH or 0.1 M HCl and a Pye Unicam Model 292 Mk2 pH meter. Mannitol (3 g) was added with (magnetic) stirring and the resulting pH (about 2-3) was increased to the predetermined end-point (pH 8.0) by rapid titration with a suitable standard carbonate-free solution of alkali. Results were calculated according to normal practice⁹³. The method appeared to be unaffected by the presence of traces of organics or other impurities and normally gave an (estimated) precision of $\pm 0.5\%$.

Colorimetric method: The following procedure was used for each sample and standard, 4-10 standards and samples being treated simultaneously. A 1.0 cm³ aliquot of borate solution (0.1-5 ppm B) was placed in a 15 cm³ polythene tube (to avoid dissolution of boron from glass) complete with a close-fitting lid. Two cm³ concentrated HCl and 3 cm³ of 10% EHD in chloroform were added before shaking the mixture carefully for 1 minute to extract the boron into the organic phase. After a 1-2 min settling time, a 0.50 cm³ aliquot of the (lower) organic layer was removed by means of a dry Aglar microsyringe and placed in a dry soda-glass volumetric flask. One cm³ 0.375% curcumin in acetic acid was added to the chloroform solution, resulting in a dark red mixture

containing the boron complexes, and 0.30 cm^3 concentrated H_2SO_4 was also added to aid their complete formation by removal of water. The reaction was allowed to proceed for 15 minutes and then the mixture was diluted to the mark (25 cm^3) with absolute alcohol. Small quantities of the resulting orange-coloured solutions were measured for absorbance at 550 nm using 1 cm quartz cells in conjunction with a Perkin Elmer 124 spectrophotometer. A typical set of results is shown in Figure 3.2.

The method could be reproduced to about $\pm 5\%$ with difficulty; major sources of error encountered are explained further on.

3.2.2 Metal assay

Analyses of sodium, calcium, magnesium and potassium were carried out by Atomic Absorption Spectrophotometry using a Hilger and Watts' Atomspek instrument. The methods and standards employed were as described in the manufacturer's handbook (and summarised in Table 3.3).

TABLE 3.3. CONDITIONS FOR ANALYSIS OF Na, Ca, Mg and K by AAS

Metals	Wavelength/nm	Range of standards/ppm
Sodium	589.0	0.2 - 0.4
Calcium	422.7	0.5 - 10.0
Magnesium	285.2	0.05 - 1.0
Potassium	404.4	100 - 1000

There was no significant mutual interference of metal ions either with or without the presence of borates during assays and the

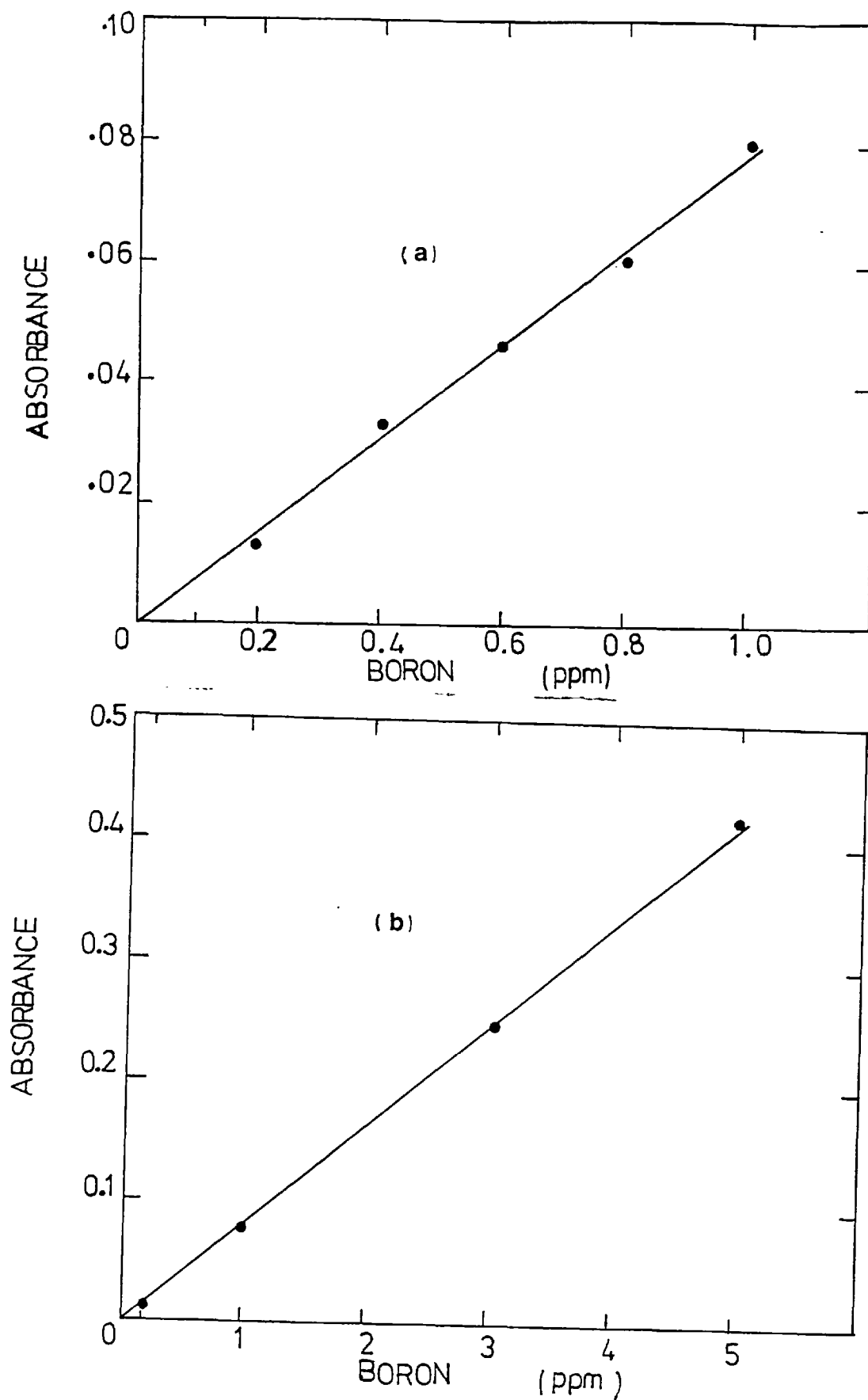


Fig. 3.2 Boron absorption calibration curves at 550 nm using 1-cm cell (a) 0 - 1 ppm B (b) 0 - 5 ppm B.

normal precision ($\pm 3\%$) was routinely achievable. Both organics - EHD and CTMP - caused major discrepancies however. These are illustrated in Fig. 3.3. To overcome this difficulty a method was adopted in which both standards and samples were made up for assay in the presence of similar quantities of organic contaminant. Thus, the water employed in preparing standard solutions was previously saturated with EHD, CTMP or a mixture of the two. Detailed experimental procedures do not need to be given here.

3.2.3 Chloride determination

Mohr's method¹¹⁰ was used for the determination of chloride ions.

Experimental

Typically, a 50 cm³ sample in a 250 cm³ beaker was adjusted to pH 7-10 with 0.05 M Na₂CO₃; 1 cm³ 5% aqueous K₂CrO₄ was added; and the mixture was titrated with 0.01 M AgNO₃ to the first pale brown colour, diluted to 100 cm³ and titrated to the end point. Results were calculated as in Kolthoffs' book¹¹⁰.

3.2.4 CTMP determination

Spectrophotometric methods were developed for this determination in both aqueous and petroleum spirit media. As Figure 3.4 shows CTMP has three absorbance bands in the ultraviolet region. These are centred at 285, 220 and 200 nm, the latter being the most intense. Various solutions of interest were made up in petroleum spirit (see

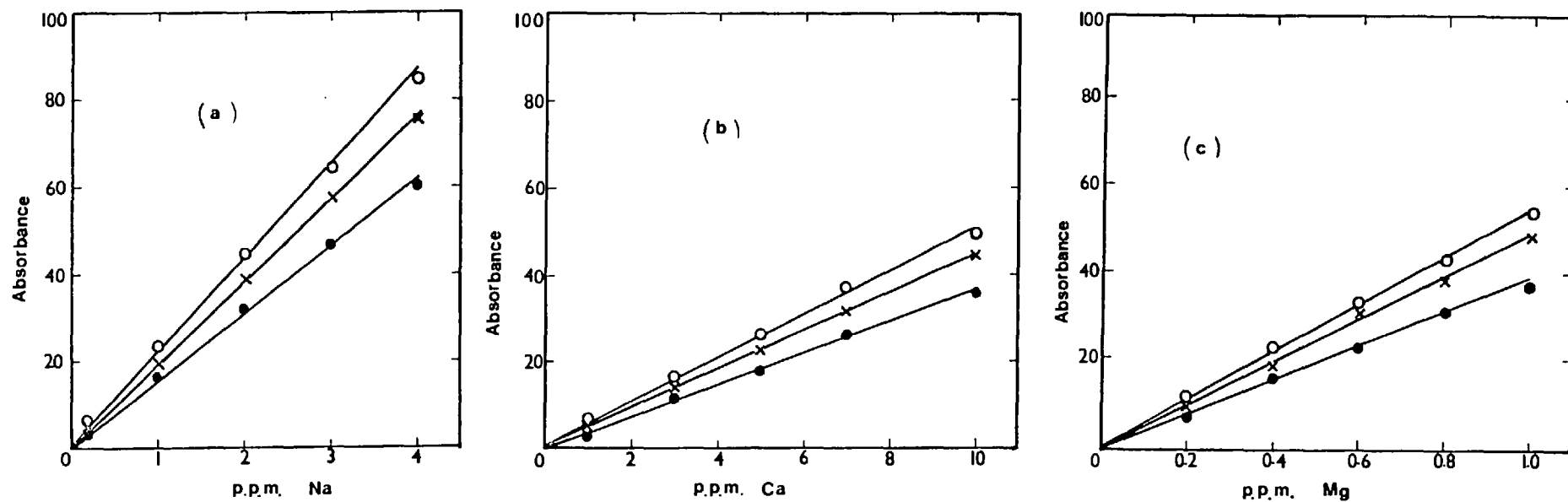


Fig. 3.3 Effect of EHD (●) and CTMP (○) on analysis of metal ions by AAS.

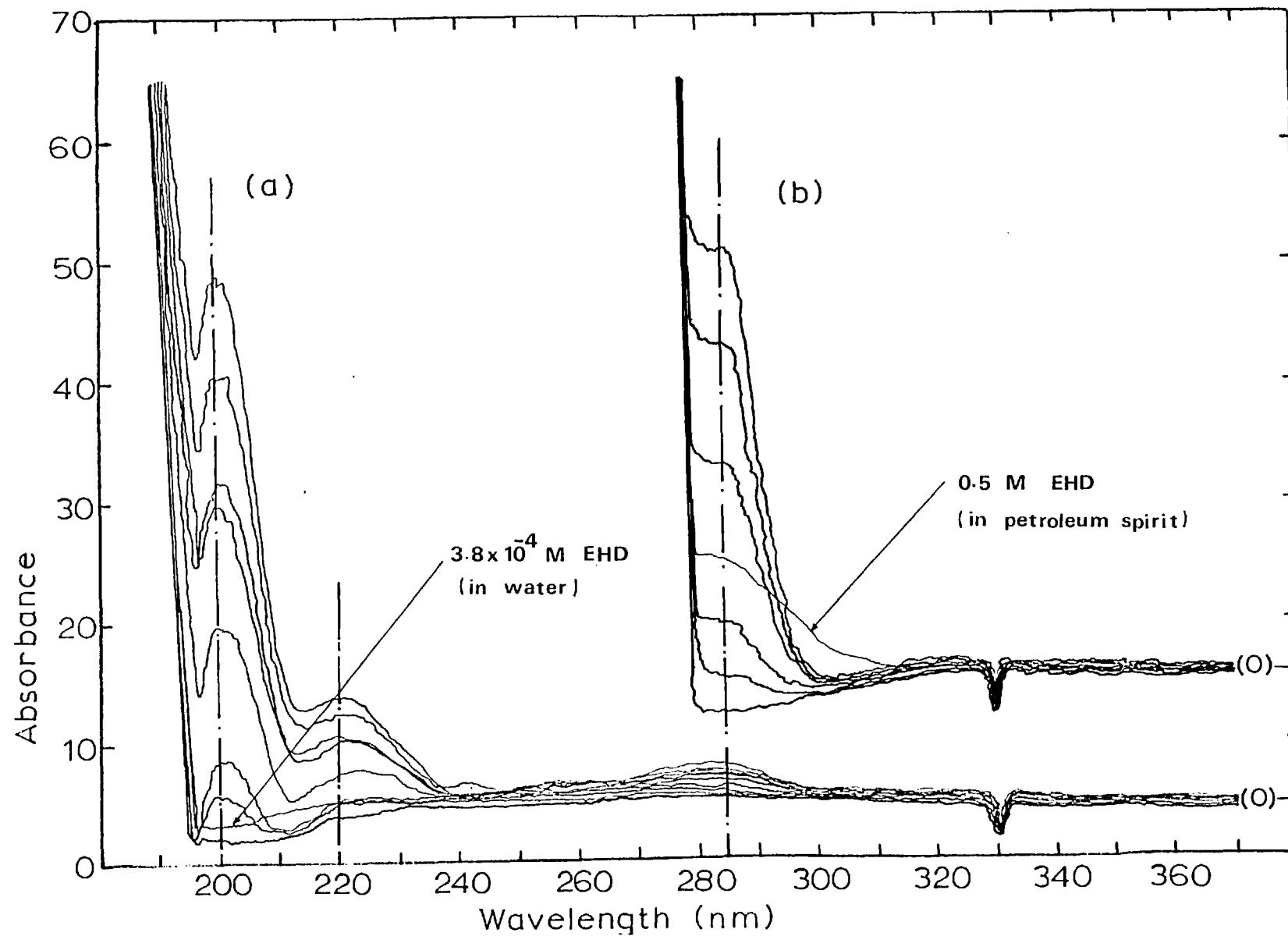


Fig. 3.4 UV spectra of CTMP in water (a), and CTMP in petroleum spirit (b).

Chapters 4 and 5) which absorbs strongly at wavelengths below 280nm; thus, only the peak at 285 nm is suitable in these cases. Figure 3.5 indicates that reasonably straight calibration curves can be obtained in the media of interest using this absorbance band at 285 nm for the range 0-30 ppm CTMP (in petroleum spirit) and that at 200 nm for the range 0-6 ppm CTMP (in water). It should be noted (see Chapter 5) that the solubility of CTMP in water is too low for the band at 285 nm to be useful.

Experimental

A stock solution of 2.03×10^{-5} M CTMP was prepared by dissolving 0.01099 g of the liquid in 2000 cm³ water with intermittent shaking over a period of several days. A series of standard solutions for testing the analytical method was prepared by suitable dilution of the stock. For petroleum spirit solutions the stock was more readily prepared by simple rapid dissolution. The absorbance of these solutions was measured in the usual way using the Perking Elmer 124 spectrophotometer and spectra recorded to construct Figures 3.4 and 3.5. From these figures the extinction coefficients were deduced to be 3.9×10^4 dm² M⁻¹ (for CTMP in petroleum spirit, at 285 nm) and 2.4×10^4 dm² M⁻¹ (for absorbance = ϵcl , where ϵ is the extinction coefficient, c the molar concentration of CTMP and l the optical path length (1 cm)).

3.2.5 Attempted determination of 2-ethyl-1,3-hexanediol (EHD)

EHD does not have a band at 285 nm or thereabouts which can be used to determine its concentration (as was the case for CTMP). Indeed, there is no useful absorbance in the normal working uv range (Fig. 3.4

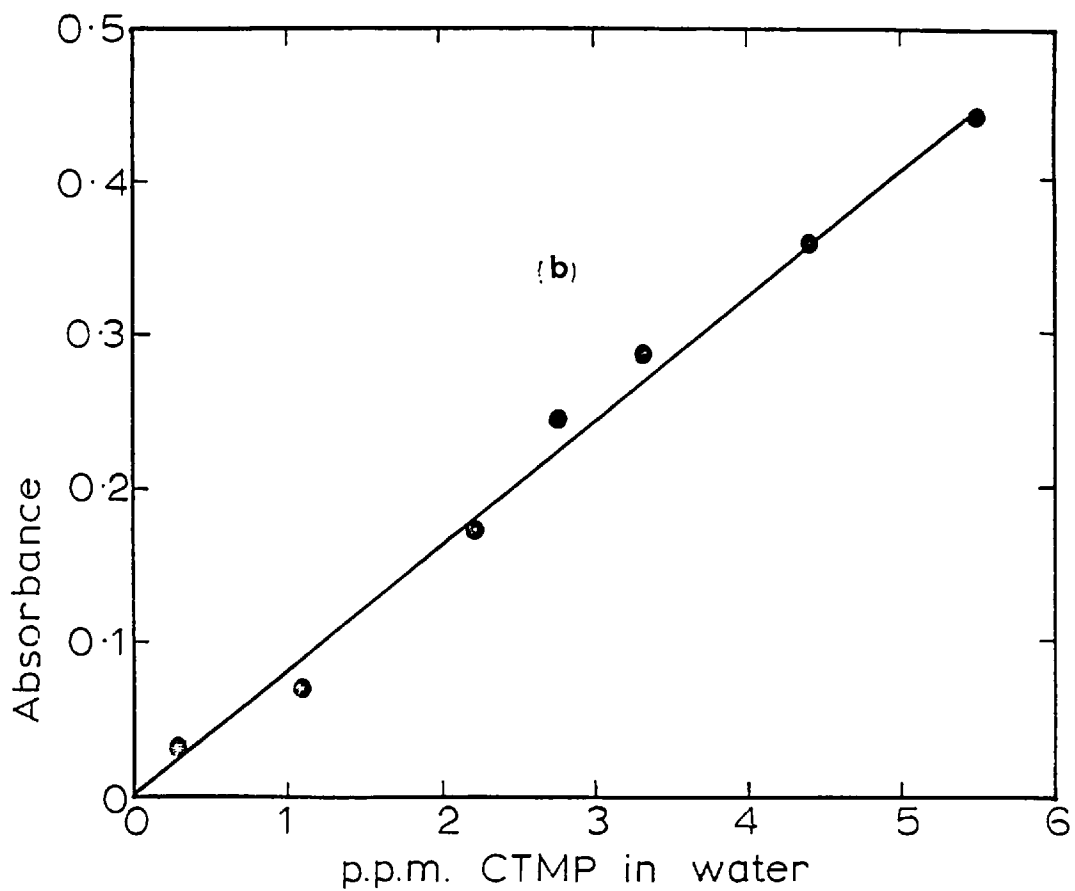
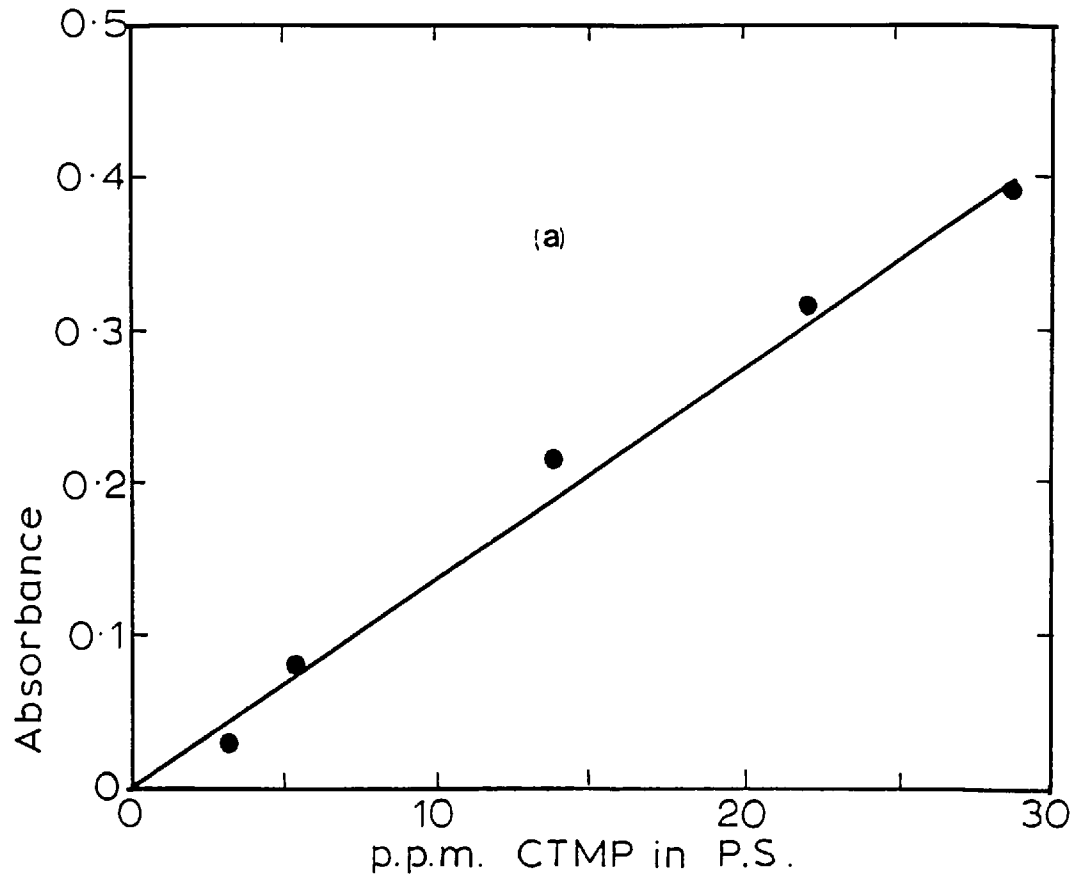


Fig. 3.5 Calibration curves for CTMP in petroleum spirit (P.S.) at 285 nm (a), and CTMP in water at 200 nm (b).

and thus uv/visible spectrophotometry cannot be employed. Attempts were made to determine the material gas chromatographically (using Perkin Elmer F30 instrument with 50 ft column) but the EHD invariably suffered thermal decomposition on the column. A literature survey did not reveal any other possibility for trial at the low concentrations encountered in the solvent extraction and therefore the assay could not be undertaken satisfactorily.

3.3 Discussion

The method described for CTMP synthesis was carried out some six times to accumulate sufficient material (about 4 dm³) for the whole work. The synthesis was time consuming (about 3 days for each batch) but was otherwise quite straightforward. The product was reasonably pure on the basis of assay figures obtained (Table 3.1) but was difficult to handle because of its high viscosity. It was therefore used as a 0.5 M solution in petroleum spirit (normally bp 100-120°C), and in order to facilitate a sufficient number of experiments with the pulse column this solution was recovered and regenerated for reuse (see Chapters 4 and 5). The appearance and properties of the solution showed no apparent deterioration over several months of use. A water solution of the compound showed no change in absorbance over a period of 1 month. Although EHD could not be similarly tested there was no evidence of any decomposition during testwork and it was therefore assumed that both solvents were completely stable.

It has been reported that the boron complexes of CTMP can be obtained in a purified crystalline form⁹² but it has not been possible to

reproduce this work here, despite many attempts under various experimental conditions. Close examination of the paper (written in Turkish) reveals that the crystalline precipitate obtained could have been borax or boric acid. The author refers to a 10% borax solution which on solubility grounds can only be prepared at elevated temperatures; on cooling such a solution a crystalline phase separates which is borax or boric acid regardless of the presence or absence of CTMP. This was established by the observation that over an extended period (overnight) approximately the starting volume of apparently unchanged CTMP or the non-crystalline boron complex had coalesced into an observable droplet beneath the crystals.

The analytical techniques described are well documented with the exception of the spectrophotometric method for CTMP. Therefore, for the most part, it is only necessary to discuss their efficiency under present conditions. No problems were encountered with acid/base or chloride determinations. The curcumin method, however, required much experience and careful selection of conditions before acceptable results were obtained. The most critical factors were the water content (which affected the stability and colour development of the chromophores, and was eventually controlled satisfactorily by introduction of the Aglar microsyringe) and ultra-cleanliness of the polythene tubes used in preparing the test solutions. In the published work¹⁰⁹ polythene tubes were used throughout but it was found here that the tubes retained boron in the surface - which was then transmitted to successive determinations, despite ordinary cleaning. Thus, the complex formation was carried out in boron-free volumetric glassware with the polythene tubes being used

only for the extraction step and being routinely cleaned by successive use of acetone, dilute HCl and water.

CTMP caused a variable increase in absorbance at the wavelengths used in the determination of alkaline earth metals by AAS (Fig. 3.3). Thus, saturated CTMP increased the absorbance by 5.5%, 13.5% and 10.0% for Na^+ , Ca^{2+} and Mg^{2+} respectively. The contamination could only be overcome by the controlled contamination of standards as described earlier. Under these conditions the method apparently worked well, but no definitive evidence for this was found. Similar comments apply to EHD although in this ^{case} the compound depressed the absorbance.

The determination of CTMP and EHD in aqueous media was hampered by their low solubilities. The methods employed therefore had necessarily to be of considerable sensitivity. No information could be found on such determinations and therefore attempts were made to develop new methods. As described earlier, this was successful in the case of CTMP, for which the aromatic molecules provided intense bands in the uv which could be used. Calibration curves indicated quite close adherence to the Beer-Lambert law and the method was therefore of considerable value for accurate determinations down to about $\pm 5\%$.

CHAPTER 4

EXTRACTION OF BORON FROM HOMOGENEOUS SOLUTIONS

4 EXTRACTION OF BORON FROM HOMOGENEOUS SOLUTIONS

The efficiency of boron extraction can be affected both by dissolved and suspended contaminants. This chapter begins with a reasoned outline of the choice of systems and methods of study as it has been considered of primary importance for the work to be of industrial relevance. The main substance of the chapter is concerned with extraction equilibria in homogeneous (clear) solutions.

4.1 The choice of systems and methods for study

Mineral chemical processes in aqueous media generally follow the scheme dissolution, purification and recovery as shown in Fig. 4.1. In the case of boron a leach solution is obtained either as a consequence

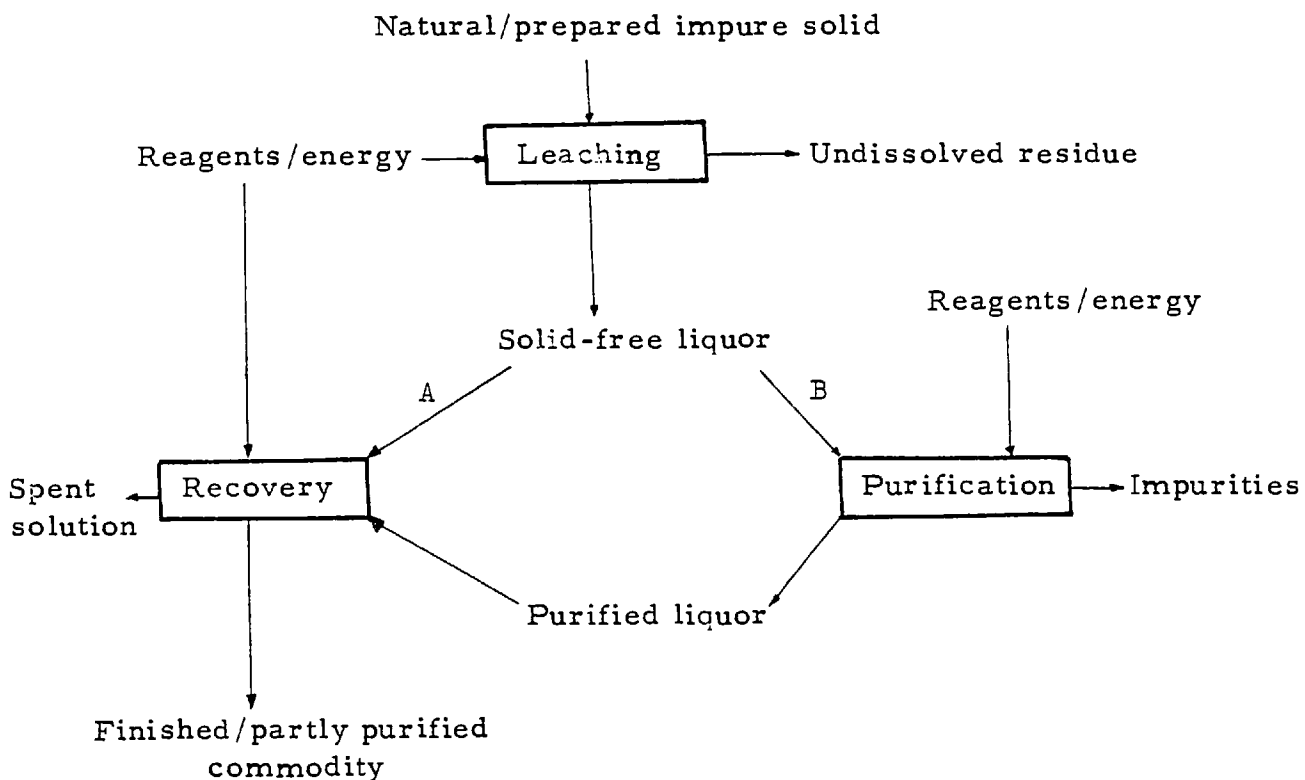


Fig. 4.1. Scheme for aqueous processing

of natural leaching or through the direct dissolution in water or acid of prepared solids. Sparingly soluble impurities are removed by solid/liquid separation and soluble impurities either by selective crystallisation (Route A) or solvent extraction (or ion-exchange) (Route B). There are no other important industrial methods for upgrading primary boron commodities. The high solubility of certain boron compounds generally causes a considerable quantity of boron to be lost in the plant-end liquors. For the purpose of 'cleaning' these liquors the purification step involves the selective removal of boron and any other obnoxious contaminants to leave an environmentally acceptable effluent. Although in principle this could be effected by such methods as distillation and selective precipitation, in practice only solvent extraction and ion exchange are economic possibilities.

Table 4.1 shows some of the relative merits and disadvantages of solvent extraction and ion exchange which are of particular relevance to boron and uranium. The table includes references to pulps but does not consider cation exchange.

As can be seen the choice between solvent extraction and ion exchange as techniques for purifying solutions is not clear-cut: in a general way, to achieve high capacity in an automated continuous plant solvent extraction is preferable in principle, but if efficient solid-liquid separation is difficult, or the solutions are particularly dilute (perhaps a few ppm), then ion exchange might be preferred. When considering cations solvent extraction often has better selectivity⁷⁵ but with anions this difference largely disappears. In the present case (of boron

TABLE 4.1. RELATIVE MERITS AND DISADVANTAGES OF SOLVENT EXTRACTION (SX) AND ANION EXCHANGE (IX)

Merits	Disadvantages
SX and IX are selective for anions ^{68,75}	Soluble and entrained solvent loss (SX) ^{111,112} and attrition and suspended loss (IX) ⁷⁵
SX is suitable for large scale continuous operation in automated plant	IX is only generally suitable for batch or semi-continuous operation on a smaller scale. Continuous IX is new technology yet to make an impact industrially ⁷⁵ .
IX circuits can tolerate a small proportion of solids thus reducing the need for solid/liquid separation and allowing pulps to be processed ^{113,114} .	SX tends to produce CRUD at interfaces and leach liquors generally require careful clarification before contacting with organics ¹¹⁴
	IX resins are subject to poisoning; SX solvents and diluents are combustible.
SX and IX generally have low operating costs ¹¹⁴ .	SX and IX are capital intensive..

effluent) the major factors are high throughput (about 50 tonne per hour); cheapness of operation; and ability to handle entrained solids while reducing the boron concentration to below 5 ppm.

Boron specific resins have been developed⁶³ (see page 30)

but, owing to the stability of the ion pairs and to the basic nature of the amine salt exchange groups, elution of the boron is inefficient when

water at neutral or basic pH is used, and when acid is used large quantities are consumed (by the N groups). Conversely, some success has been claimed (though the results are in dispute), for solvent extraction in pulp- that is, Ritcey et al.,¹¹⁴ have suggested conditions under which uranium can be successfully treated by the system tertiary amine/ O.1 M kerosene in the presence of 30-35% solids. Various other papers have appeared^{115,116} on this subject. For these reasons, it was decided to concentrate on an investigation of the solvent extraction technique in purifying borate liquors in the present work.

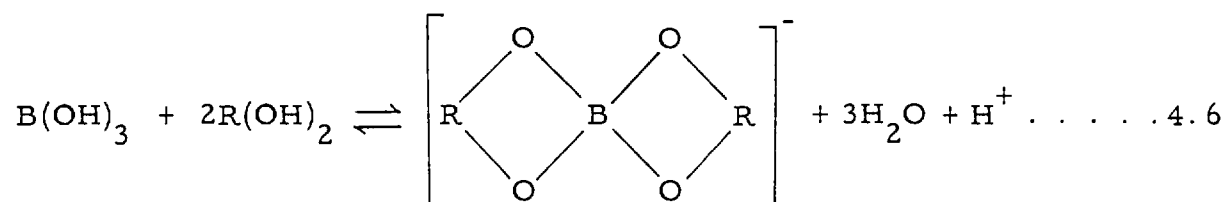
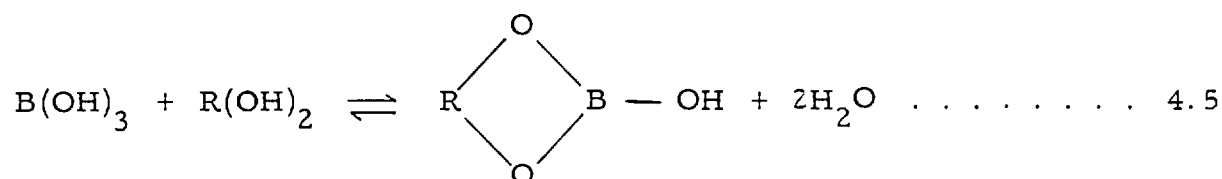
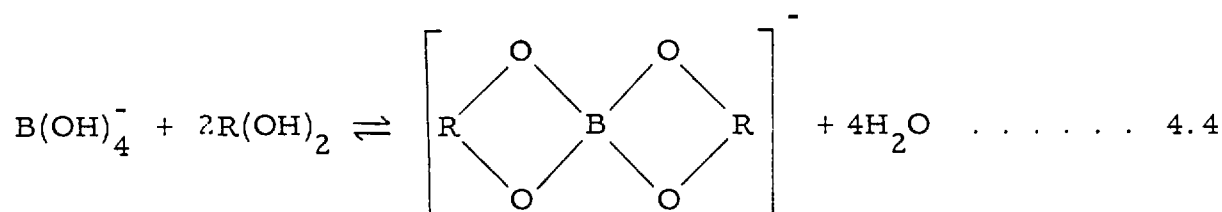
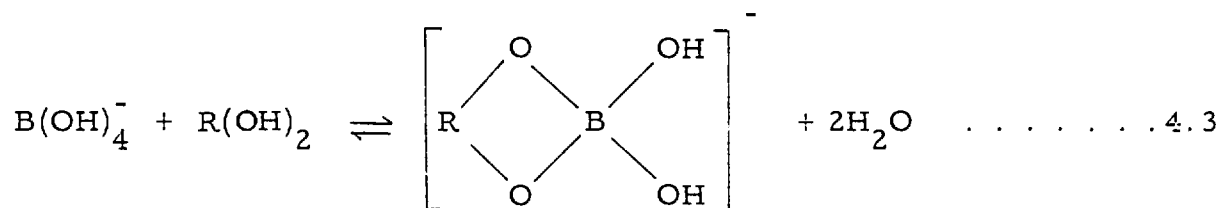
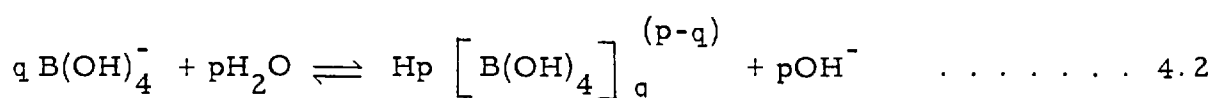
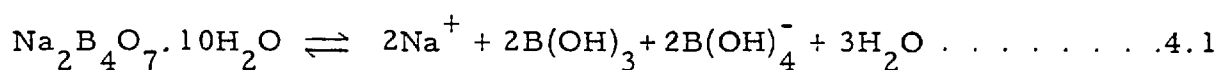
Various organic molecules complex strongly with boron to form species which have much greater solubility in petroleum-based solvents than in water. This field of complex chemistry is dominated by the boron-oxygen bond which is exceptionally strong ($104-130 \text{ kcal mol}^{-1}$)¹¹⁷ in both the tetrahedral and trigonal planar configurations. The molecular dimensions of organic 1,2 and 1,3 diols are precisely suitable for the formation of unstrained 5 or 6 membered rings respectively in these configurations, and therefore the field is also dominated by such diols. Many papers have appeared on the reaction chemistry of boron with diols and other substances and on their extraction into organic media.

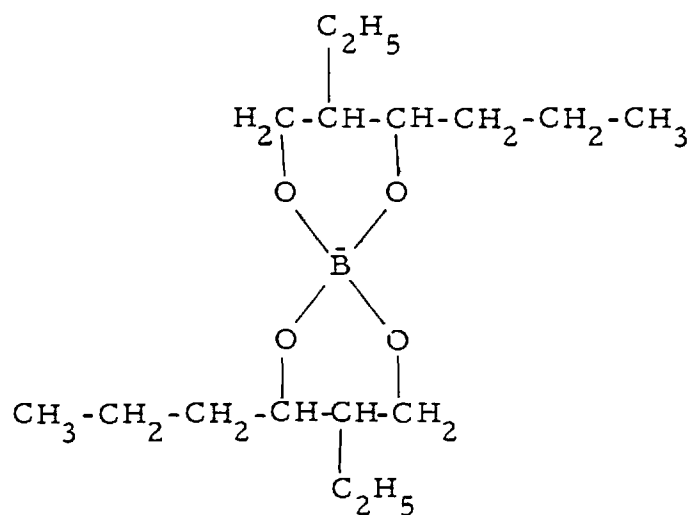
Thus, Vinogradov and Azarova¹¹⁸ mention some 22 papers devoted to the extraction of boric acid from aqueous solutions by organic solvents immiscible with water and themselves report a comparative study of the extraction efficiency of a variety of different solvents, including ordinary alcohols (such as n-butanol) and complex phosphates (such as di-isopentyl methylphosphate). Dyrssen and Uppstrom¹¹⁹, in particular,

chose the aliphatic 1,3 diols such as 2,2-diethylpropane-1,3-diol and 2-ethyl-1,3-hexanediol (EHD) for a detailed study of the equilibria involved, and, indeed, the latter substance is generally the reagent chosen as most efficient for use in analytical determinations of boron^{98,99,100,107,109}. A number of patents^{90,120,121} and papers^{122,123} covering the reactions with a wide range of polyols have been published. Garrett¹²⁴ refers to EHD, noting its high selectivity in acid medium but rather less satisfactory solubility in water (4.2% by weight). He also considers⁶⁸ some 25 aromatic diols and triols listing preferred solvent carriers, extraction efficiency, stability and qualitative relative water solubility, and suggests that these substances are especially selective for borates in alkaline medium. Kemp¹²⁵ filed results of similar investigations. From these patents it is evident that the 1,3 diol 2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylphenol (CTMP) has relatively favourable characteristics: (1) it extracts more efficiently at the alkaline pH (about 9) found in naturally occurring brines, (2) it is stable and very sparingly water soluble and (3) the extraction efficiency is relatively high. Conversely Grinstead¹²⁶⁻¹²⁸ concentrates on 1,2 aromatic diols such as 4-tert-butyl catechol (TBC) in admixture with alkyl ammonium salts or higher alcohols with which selective extraction of boron and calcium together can be achieved in the presence of magnesium and chloride ions. Grannen¹²⁹ and Peterson¹³⁰ patented a list of salicylic acid derivatives such as 5-tertiary-octyl salicylic acid, and claimed that they would selectively extract boron at both acidic and alkaline pH values, but in the examples given only about 50% of boron could be transferred in a single stage.

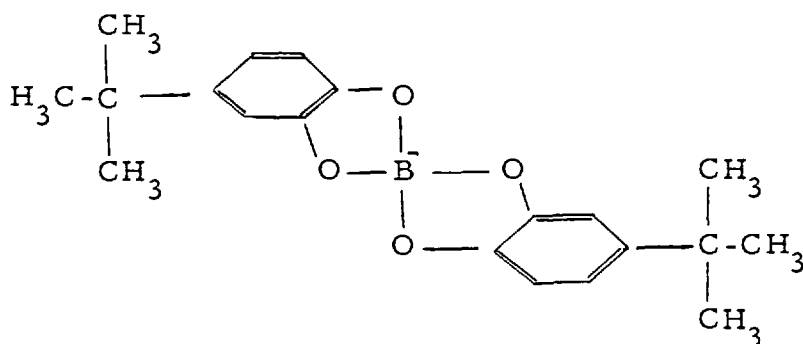
The diols mentioned above can be used to represent three different types of reaction with boron species and one of each (EHD, TBC and CTMP) was selected for study. Relevant structures are shown in Fig. 4.2 and general equations are given below.

Complex formation between boron species and polyols can occur in a number of ways^{69,127,131,132}, the most important being⁹⁰ the extraction from alkaline solutions as an ion-pair (borate didiol ester, $B(O_2R)_2^- M^+$, or polyborate ester) and from acidic solutions as the boric acid associate complex or ester, $B(OH)_3 \cdot n(OH)_2 R$.

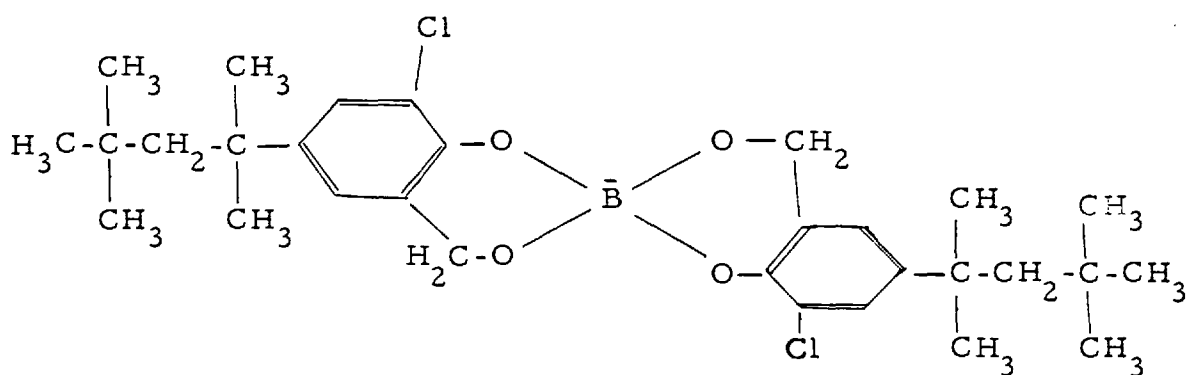




(a) 1 : 2 Boron-EHD complex



(b) 1 : 2 Boron-TBC complex

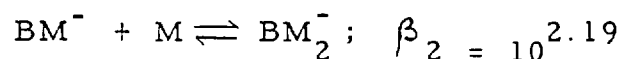
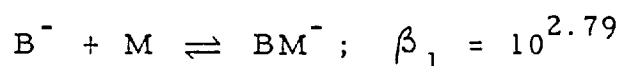


(c) 1 : 2 Boron-CTMP complex

Fig. 4.2. Structures of three types of boron-diol complexes.

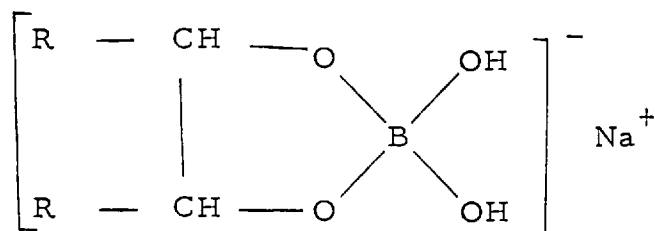
{ Only 1 : 2 (boron-to-diol) complexes are shown).

Dissolution of, say, borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in water, sets up the equilibrium in equation 4.1. The simple ions so formed undergo various polymerisation or condensation reactions¹³³⁻¹³⁶ such as those referred to in equation 4.2 and may further react according to equations 4.3 - 4.6 in the presence of polyols. The equilibrium positions are generally dependent on pH as is clear from equations 4.2 and 4.6. Much work has been published on these reactions but although constants are available¹³³⁻¹³⁶ for some of the species implied in equation 4.2 and for some of the organo-boron complexes¹¹⁷ (equations 4.3 and 4.6), they are not generally available for the other equations except in certain simple cases such as complex formation with mannitol^{137,138}, where the products are water soluble. Thus, for the reactions (cf. equations 3.1, 4.3 and 4.4).



where B^- and M are the borate ion and mannitol ($\text{CH}_2(\text{OH})(\text{CHOH})_4\text{CH}_2\text{OH}$) respectively.

As can be seen from equations 4.1 - 4.6 borate equilibria can be very complex and a number of different compounds besides boric acid and borax can be isolated in the solid form. Dale¹³⁹⁻¹⁴¹ reports the formation of various crystalline phases, such as



but states that in many cases the hydrolytic stability of these substances and their corresponding esters is low.

Figure 4.3¹⁴² shows the relative proportions of certain boron species in water of various pH's. From this figure, it appears that although in dilute solutions (less than 0.2M borax) at alkaline pH the

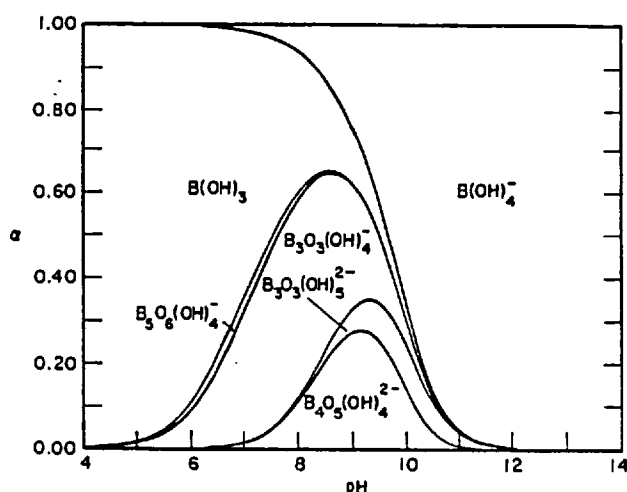


Fig. 4.3. Distribution of boron among various ions¹⁴² (total B_2O_3 concentration 13.93 g l^{-1}) At a given pH, the fraction, α , of the total boron present as a given ion is represented by the portion of vertical line falling within the corresponding range.

dominant species is $B(OH)_4^-$ and at acidic pH it is $B(OH)_3$, at intermediate values a considerable number of species coexist at significant concentrations. It is not considered helpful here to study these equilibria in detail but rather to concentrate on reactions between a representative species

(i.e. $B(OH)_4^-$ or $B(OH)_3$) and the polyols.

Although the only plant currently in use for borate solvent extraction relies on mixer-settler designs, it is important to consider also the other possibilities for contacting and separating immiscible phases. In addition to mixer-settlers¹⁴³⁻¹⁴⁹ reports have appeared on the design of spray columns¹⁵⁰, pulse columns^{151,152}, packed columns^{150,153,154}, rotary-film contactors¹¹⁶, centrifugal contactors¹⁵⁰, hydrocyclones^{150,155}, ultrasonic contactors¹⁵⁶, etc. Mixer-settlers have the advantages of simplicity, proven reliability in industry, and ease of achieving long contact times when the kinetics of reaction are slow enough to warrant it¹⁴⁵. Gravity flow may be used throughout and when, as in the case of uranium extraction, shielding may be required this is relatively inexpensive to install¹⁴⁴. The plants are flexible in operation and amenable to theoretical modelling and ready calculation of stage efficiencies¹⁴⁴. They are almost universally used in the mineral industry but tend to occupy a large ground area¹⁵⁰ and lead to the formation of emulsions and crud (owing to the mode of agitation) especially when pulps are considered. There is little available information about the relative merits of the other contactors mentioned and they have little or no industrial use at present in metallurgical solvent extraction. However, Pratt¹⁵⁰ provides two detailed articles on the theory and practice of liquid-liquid extraction which compares a variety of stagewise and differential contactors and stresses the self-cleaning action of the pulse column when operating in the presence of solids. Columns have the advantages in principle of multistage operation in a single (space-saving) column, and provision of efficient contact between phases without vigorous

agitation, but they involve complicated design and operation in addition to being less suitable than mixer-settlers in the respects mentioned above. It has however been reported¹⁵² that in solvent-in-pulp treatment by sieve-plate-pulse columns lower solvent losses can be achieved than with mixer-settlers, and that¹⁵¹ the sieve plates allow a shorter column length for a given capacity than that required in an analogous packed column.

In these circumstances, it was decided to undertake experiments with both a mixer-settler and a sieve-plate-pulse column on the laboratory scale. In both cases, new equipment was designed but in the former case the mode of operation was often conveniently reproduced in ordinary shake-out flasks. A comparison of the operating characteristics of these items of equipment was made together with more intensive experiments to study the extraction efficiency of boron in the presence of the various soluble contaminants - Ca^{2+} , Mg^{2+} , Na^+ , Cl^- - which might be expected to be present in boron-containing effluents.

4.2 Apparatus

Figures 4.4 and 4.5 show respectively the mixer-settler and sieve-plate contactors which have been constructed. The mixer-settler design was based on that of Lawson¹⁴⁹ and the contactor was constructed from Pyrex glass beakers of 250 and 600 cm³ capacity. In order to provide a controlled environment each mixer had a double skin made by sealing one beaker inside the larger one so that thermostatted water could be recirculated; the top of the apparatus was flattened and sealed (Araldited) with a circular perspex sheet (1.0 cm thick) fitted with

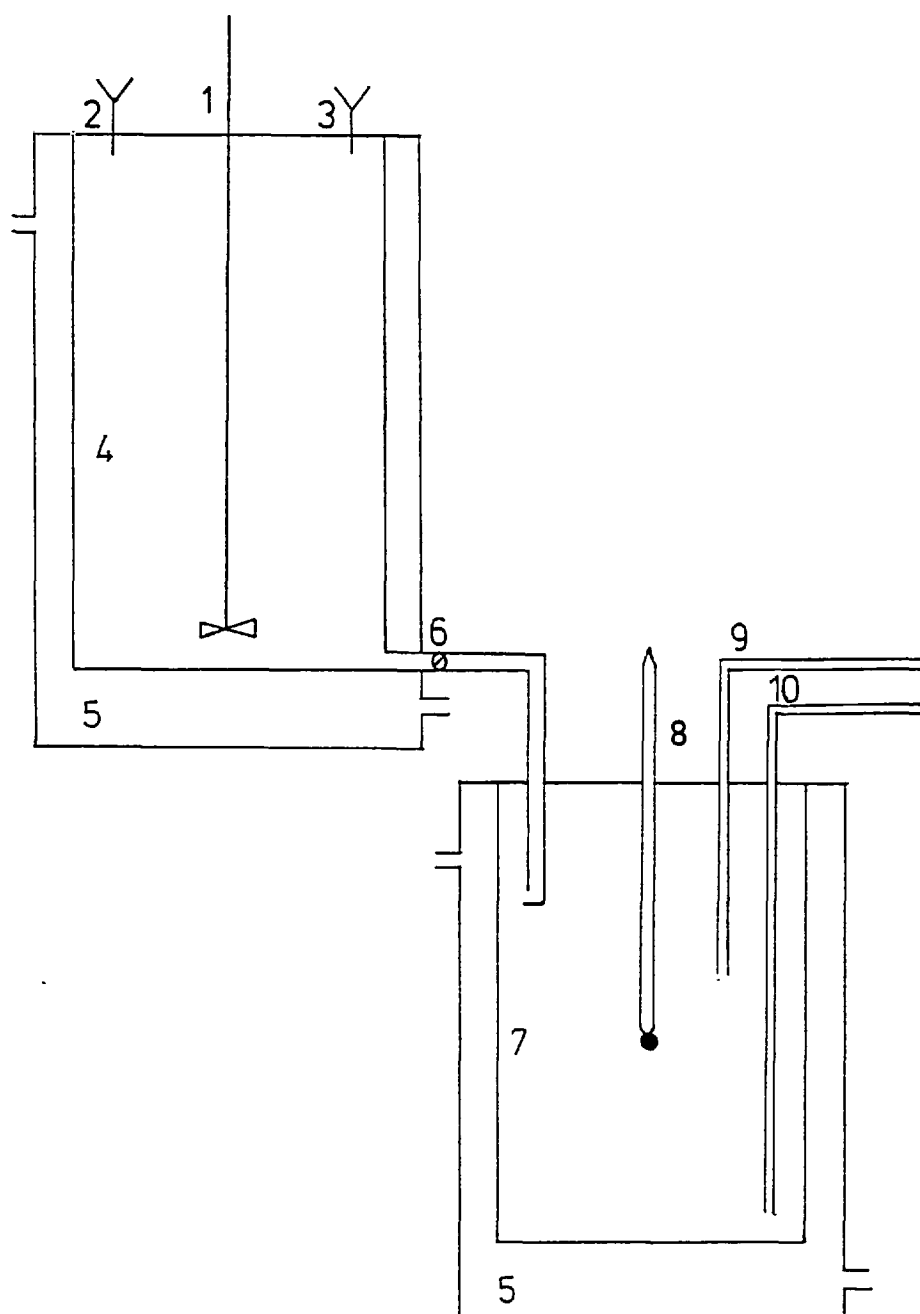


Fig. 4.4. A laboratory mixer-settler.

1. mechanical mixing, 2. aqueous phase inlet,
3. organic phase inlet, 4. mixing vessel, 5. water jacket, 6. mixed phase port (tap), 7. settling vessel,
8. thermometer, 9. organic phase sampler and 10. aqueous phase sampler.

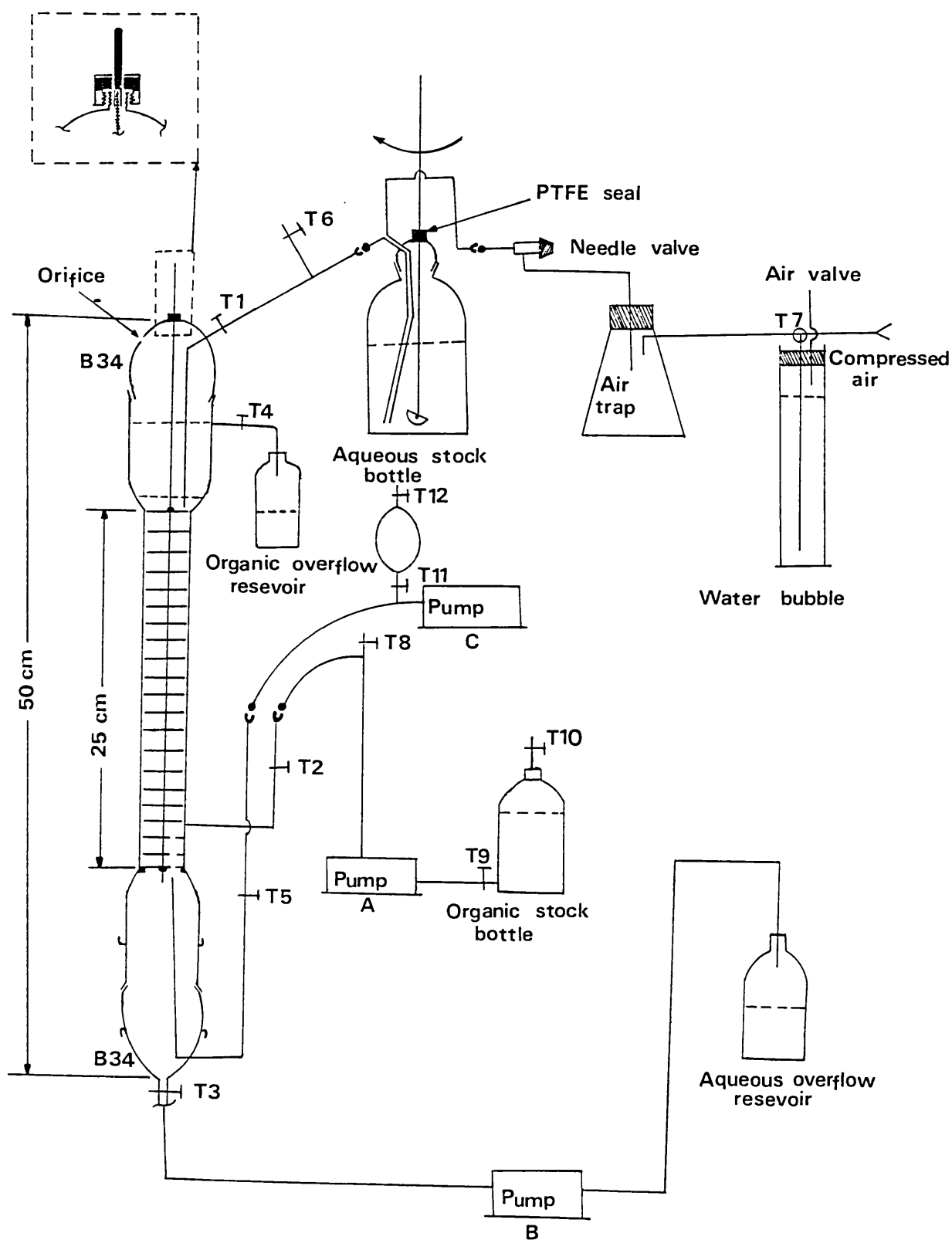


Fig. 4.5. A laboratory sieve-plate-pulse column.

2 x B10 and 1 x B24 Quickfit stoppers for access in feeding, pH adjustment and stirring; and the base of the inner surface was gravity connected via a tube and teflon tap to a similarly constructed settler. The latter had 4 x B14 Quickfit stoppers for access in feeding, temperature measurement and organic and aqueous phase sampling.

The sieve plate pulse column was designed on the basis of two publications^{151,152} and was also made essentially of Pyrex glass. The main construction was a vertical tube 25 cm in length and 2.5 cm internal diameter having B34 cones and sockets at either end (as shown in Fig. 4.5) and giving an overall length of 50 cm. The tube contained a stainless steel rod 44.5 cm in length and 0.2 cm diameter carrying 23 horizontal teflon disks (each of 2.5 cm diameter, 0.15 cm thick and having 42 x 0.2 cm randomly drilled holes) spaced at 1.0 cm intervals by means of stainless steel tube spacers. The rod assembly rested on glass jags at the base of the 25 cm tube and was retained at the top by a centralizing control head shown in the inset to the figure. As can be seen the upper part of the rod was threaded to allow the disks to be clamped in position (with the aid of a stainless steel nut and 5.0 cm spacer), and it was also threaded at the base for a similar purpose.

There were six access points to the column in operation, five of which were governed by glass taps T1-5 and the sixth being merely an orifice for equalizing the pressure above the liquid phases. T1 controlled inletting of aqueous feed and was connected via the tee junction at T6 (for removal of air bubbles) and a 4.0 mm Quickfit ball and socket joint to the 2 dm³ aqueous stock bottle. This bottle was fitted with a custom-built B34 head to facilitate sealed stirring (mechanical

stirrer, Comtex Ltd., London) and pumping of solutions and slurries, and was connected via a second 4.0 mm. ball and socket joint to a Rotaflo TF6/13 glass needle valve to an air trap, water bubbler (carrying three-way tap, T7) and compressed air source, the latter items having plastic tube connections. T2 similarly controlled inletting of organic feed from the 1 dm³ stock bottle (having access taps T9 and T10) by means of a piston micro-pump A (Rlaxon Ltd., London) fitted with a screw micrometer (T8 was for air bubble removal). T3 provided the aqueous phase outlet and was connected to a second piston micro-pump B (Distillers Company Ltd., Surrey) and a 1 dm³ aqueous underflow reservoir by means of plastic tubing. T4 facilitated direct run-off to the 1 dm³ organic overflow reservoir. The pulsing action of the column was provided by a diaphragm pump C ('Cub' motor, Hydraulomat Ltd., London) and inletted via a tee junction (carrying a 100 cm³ bulb between two taps T11 and T12, for modifying the pulse sharpness and removing air bubbles), 4.0 mm ball and socket joint and T5.

The precise configuration and positions of the ends of the inlets to and outlets from the column were critical (see later) and, thus, the pulse inlet (T5) reached just to one side of the centre of the rod-base retaining nut; the inlet via T2 was precisely horizontal (to avoid hold-up of liquids); the aqueous inlet (T1) extended to just below the liquid interface (which itself was maintained about 0.5 cm above the uppermost disk); and the organic overflow (T4) was situated as far as possible above the interface (to give the maximum settling height and volume (10 cm and 120 cm³ respectively)). Also important in the design was the dead height and volume beneath the disks (12.5 cm and 150 cm³

respectively, which functioned as an aqueous settler).

Figure 4.5 relates to open-circuit operation. A separate head (at T1) was also provided for closed-circuit operation. In this case T1, the head and all apparatus connected on the right hand side of it were removed and replaced by a similar construction facilitating direct connection of the tube from pump B.

Experimental

Typical modes of operation of the mixer-settler, shake flasks and pulse column are described and compared below. Data obtained during the development of parameters for the column are also described.

Mixer settler: Equal quantities (50 cm^3) 0.463 M B (as borax) solution and 1.7 M EHD in petroleum spirit (100/120) were placed in the mixer (4) via inlets (2 and 3 respectively) (Fig. 4.4) with tap (6) closed. Tap water was passed through the water jacket (5) via a long copper coil immersed in a Gallenkamp Ltd. thermostat bath maintained at $25 \pm 1^\circ\text{C}$ (which typically provided a constant temperature of $20 \pm 1^\circ\text{C}$ in the settler as observed on the thermometer (8)). The layers were equilibrated with stirring for 15 minutes with intermittent adjustment of pH to 5.4 (by momentary insertion of a combined pH electrode), and were then allowed to run off to the settler (7) via the tap (6). The phases settled out over a period of 0.5 hour and samples of the clear solutions were withdrawn through (9) and (10) with the aid of a suction bulb into 25 cm^3 conical flasks. The aqueous layer was analysed according to the acid-base method (Chapter 3).

Figure 4.6 shows the results of experiments to determine an equilibrium curve for the extraction of boron and provide a comparison of the operation of the mixer-settler and shake flasks. In these experiments the phase ratio was systematically changed as in the figure to obtain the curves. These results are discussed further on.

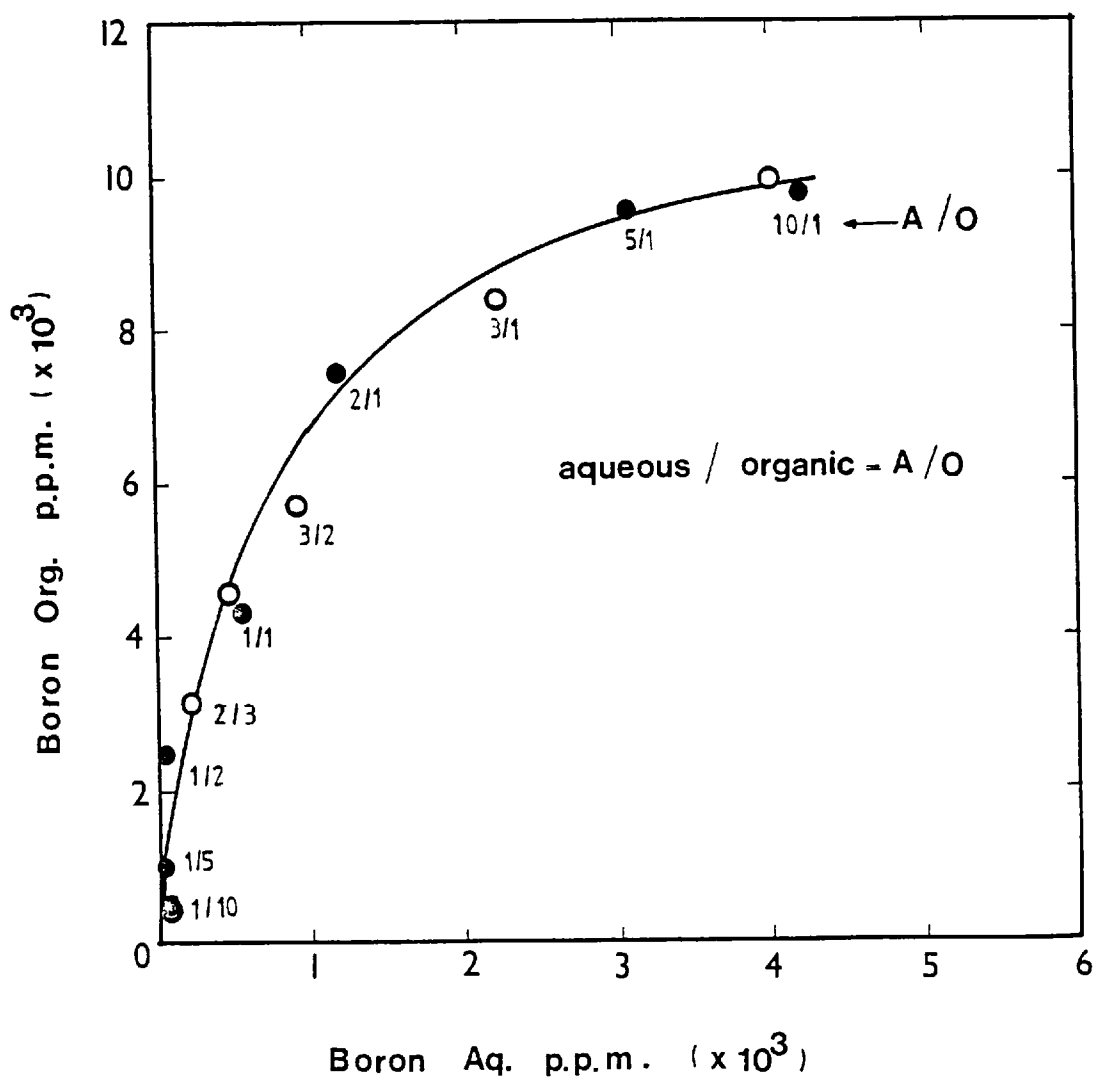


Fig. 4.6. Equilibrium curve for boron (5000 ppm) extraction with EHD (1.7M) using shake flasks (•) and a laboratory mixer-settler (o).

Shake-flasks: Equal quantities (50 cm^3) of 0.463 M B (as borax) solution/and 0.5 M EHD in petroleum spirit (100/120) were placed in a 150 cm^3 B19 Quickfit conical flask and equilibrated at room temperature by shaking (8-flask shaker, Griffin and George Ltd.) for 15 minutes. The equilibrated phases were settled for 0.5 hour before withdrawing a 25 cm^3 aqueous sample with the aid of a pipette and suction bulb. Assays were by acid-base titration (Chapter 3) and typical results are shown in Fig. 4.6.

Pulse column: Referring to Fig. 4.5, 1 dm^3 0.0463 M B (as borax) was placed in the aqueous stock bottle and 1 dm^3 0.50 M EHD in petroleum spirit (100/120) in the organic stock bottle. With T1 closed, compressed air was admitted at T7 and allowed to overflow via the water bubbler. The bulb and the tube between T12 and the base of the disks rod via T5 was filled with distilled water and T12 was closed. With T1, 2, 3, 7 and 8 and the needle valve open, and T4, 5 and 6 closed the column and tubing were filled to just below the level of T8 (to avoid aqueous phase being trapped in the organic feed line), T2 was closed, and the filling was continued with pump B on (to remove trapped air between B and T3) until the end of the aqueous feed tube (below T1) was just immersed. Pump B was stopped. With the aid of a suction bulb and with T6 open any trapped air in the aqueous feed arm was removed via that tap, and T1 and T6 were then closed. With T9 and T10 open, pump A was started and pumping continued until the organic feed arm was filled with organic phase and air-free between T8 and T9. T8 was closed and T2 opened rapidly and simultaneously to admit organic phase to the column without undue pressure build-up in the arm. T1 was opened, pump B was started, and the pumping rate was adjusted to 5.0 cm^3

per minute for pumps A and B (in accordance with known settings on the micrometer attachments which had been previously calibrated by systematic timed metering of water and organic phase into tared 100 cm³ measuring cylinders). The rate of inletting aqueous feed at T1 was also adjusted to 5.0 cm³ per minute by means of a predetermined setting of the needle valve. T5 was opened and pump C started to admit pulses to the column (at the rate of 30 per minute of 0.5 cm stroke on the column). Owing to the influx of organic bubbles into the column from T2 the upper level of the aqueous layer tended to rise; to maintain this level at a preset mark (0.5 cm above the uppermost disk), T1 was closed for a few minutes. Thereafter T1 was reopened, and timing commenced. The system was allowed to equilibrate for 1.5 hours before taking samples from the inlet to the aqueous underflow reservoir. A steady state was in fact normally achieved after about 75 minutes (see later). At the end of a run the pumps were stopped, T1, 2, 3 and 5 were closed, the circuit was broken between T3 and pump B, and the column emptied. To clean the column the head was removed and the whole assembly washed with acetone and distilled water. When changing to a different organic phase the pumps and lines were, in addition, completely cleaned with the same solvents.

For closed-circuit operation the column was filled and equilibrated as above, T1 was closed and pumps A and B stopped momentarily, the head was replaced at the upper ball and socket joint by the closed-circuit head, the inlet to the aqueous underflow reservoir was connected at that head, and the pumps restarted. For operations with slurries it was necessary to stir the contents of the aqueous stock bottle continuously. Typical results, similar in nature to those given in Fig. 4.6,

are shown in Fig. 4.7.

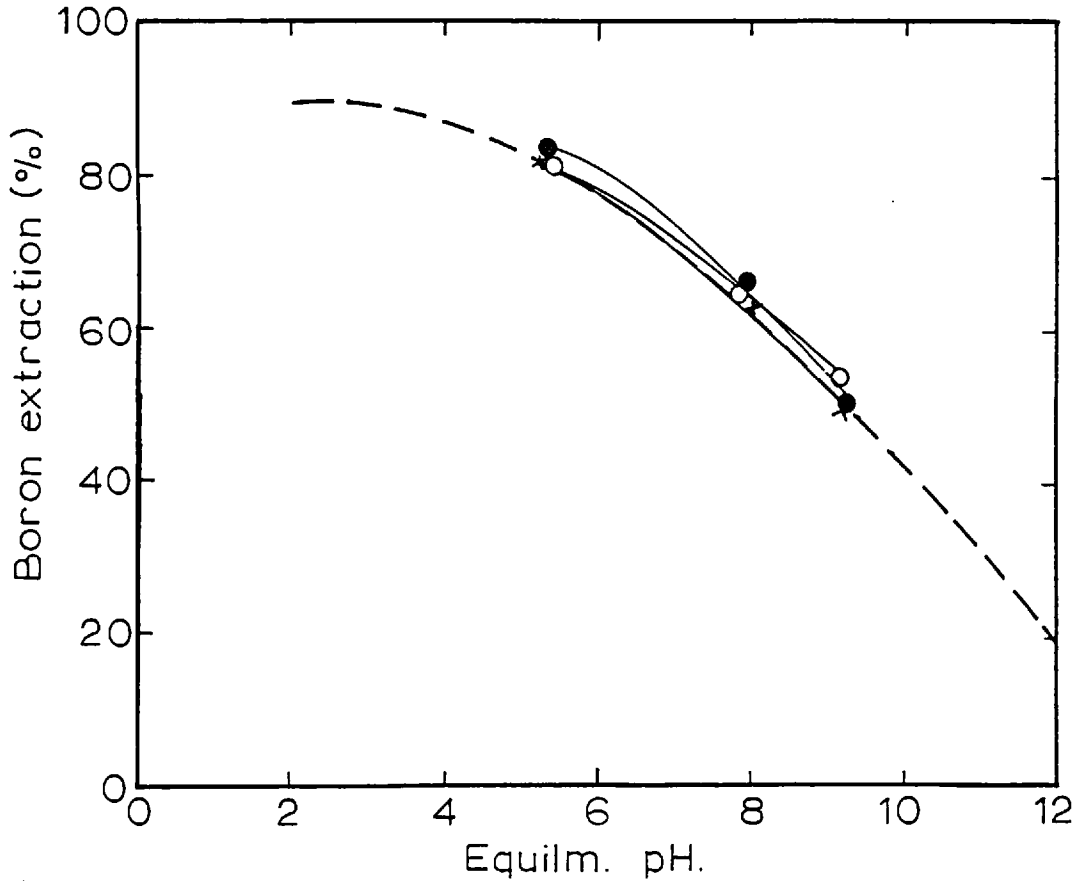


Fig. 4.7. Extraction of boron from slurries (5% solid) with EHD 0.5 M in petroleum spirit) using sieve-plate-pulse column; clear soln. (●), bentonite (o), quartz (x); (----): shake flasks exps. (clear soln.)

Optimisation of column parameters: In order to achieve the most favourable operation of the column the following parameters were altered using EHD as solvent: solution flow rates (5 or 6.5 cm³ per minute); disk spacing (1.0 or 2.0 cm) and hole diam(2 or 4 mm); sharpness of pulses and pulse stroke length (0.5 or 1.0 cm.); and the level of interface. Some of the results are given in Table 4.2.

4.3 Investigation of extraction equilibria

This section is concerned with shake-out experiments conducted under room temperature conditions with EHD, CTMP and the two solvents in admixture. TBC was also used in preliminary experiments but was later discarded owing to its rapid decomposition. The main form of data presentation is as the equilibrium curve¹⁵⁷ and as curves of % extraction against pH, time, metal ion concentration, or organic concentration.

4.3.1 Effect of contact time and pH

The kinetics of boron extraction are generally quite favourable^{98,109}, but in order to ensure adequate equilibration with the mixtures used the effect of differing time was determined. The effect of pH was expected to be more critical and this was also studied here.

Experimental

Shake-flask experiments were carried out generally as in section 4.2 but for varying lengths of time between 1 and 30 minutes at pH values of 5.3/6, 8.0/2 and 9.1/4 for 0.5 M EHD, CTMP and the two together in 1:1 ratio (i.e. 0.25 M each) in petroleum spirit (100/120). In all cases the starting boron concentration was 0.0463 M and the phase ratio 1:1. After the requisite contact-time the layers were allowed to settle only until they were just clear (2-3 minutes) before sampling and assay. Results are shown in Fig. 4.8.

A similar series of experiments was conducted at constant contact time (0.5 hour) and at 8-10 values in the range pH 2-12. As the reactions were pH dependent it was necessary (in order to achieve a

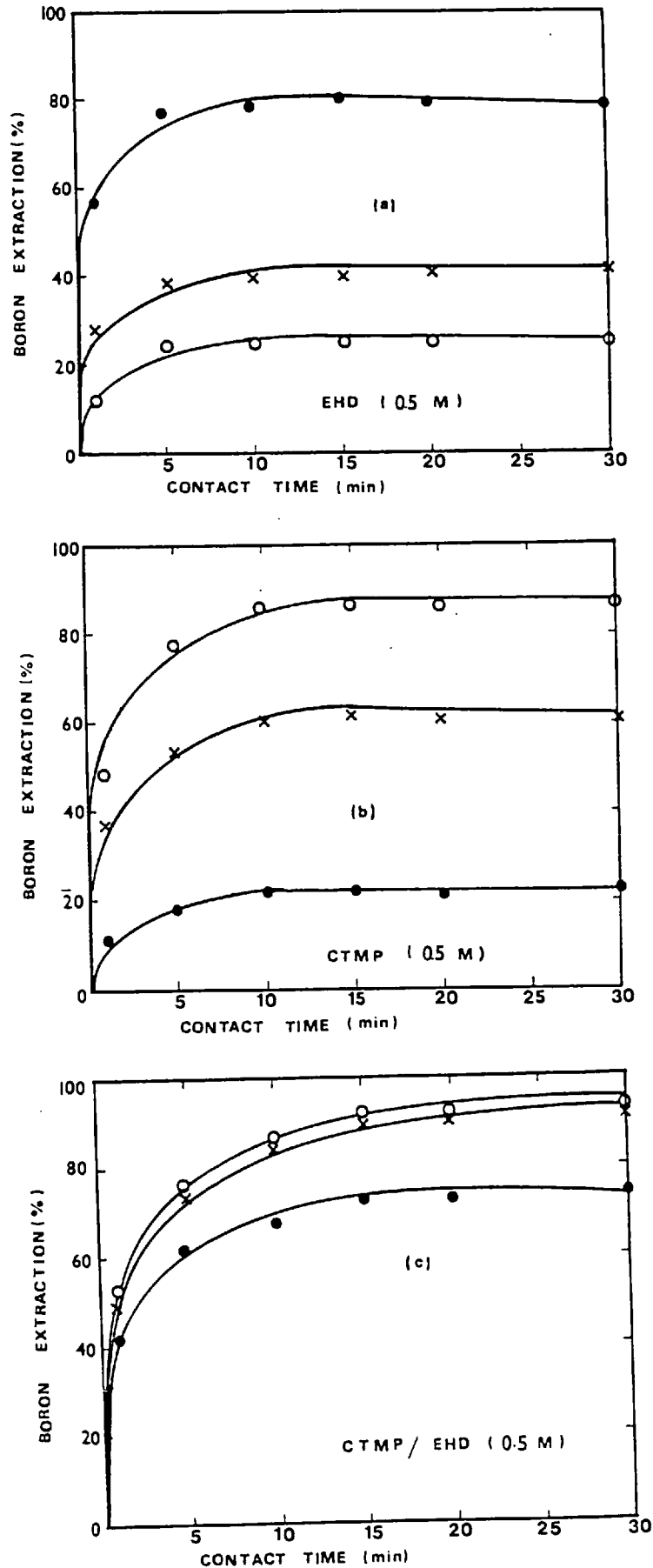


Fig. 4.8. Equilibrium time needed in extraction of boron (500 ppm) with EHD (a), CTMP (b) and CTMP/EHD (c) at pH values of 5.3/6 (●), 8.0/2 (x) and 9.1/4 (o).

particular equilibrium pH) to make intermittent pH measurements with additions, as necessary, of small volumes of either 0.1 M HCl or 0.1 M NaOH, with re-equilibration. Results are given in Fig.

4.9.

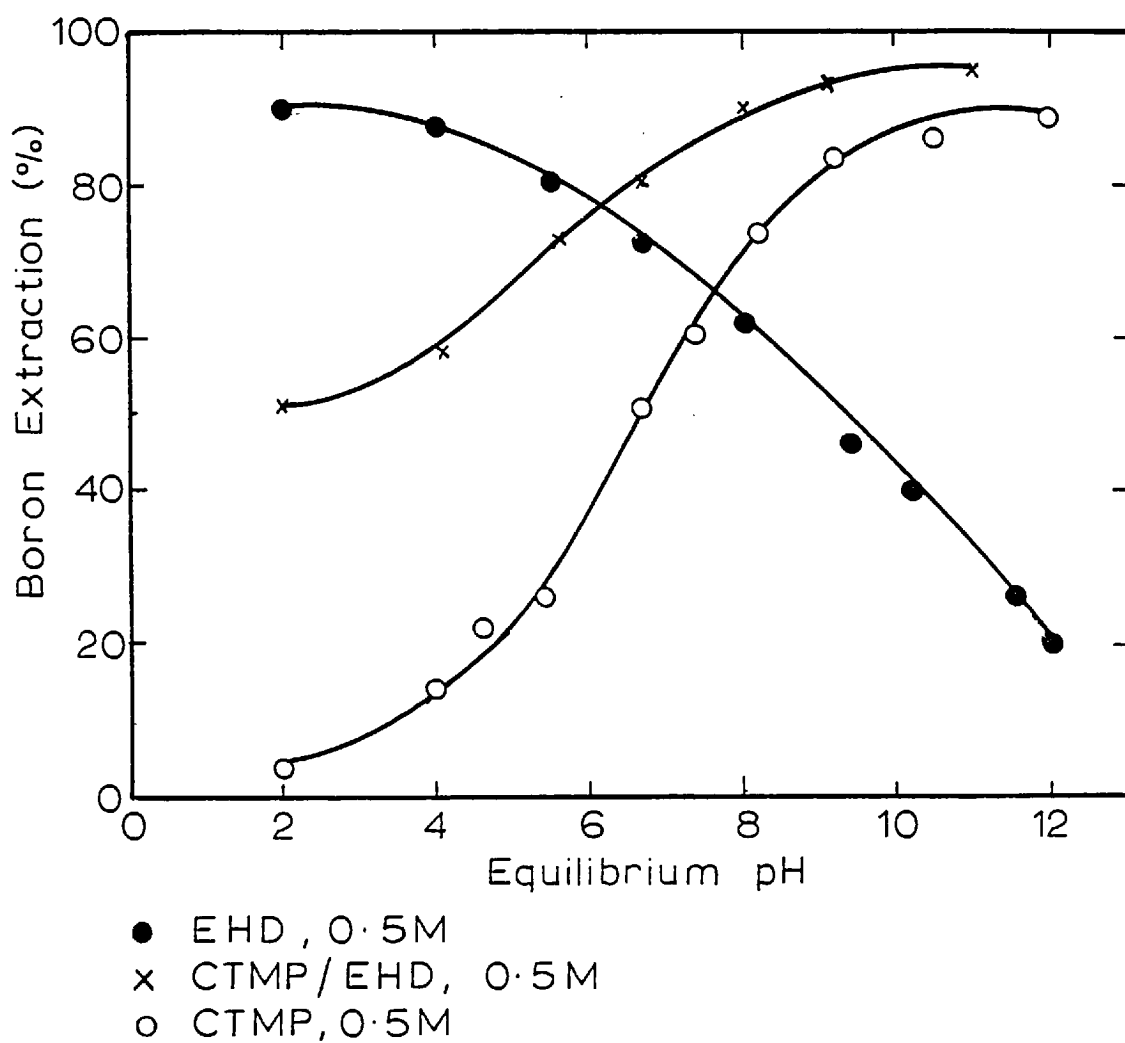


Fig. 4.9. Effect of equilibrium pH on extraction of boron (500 ppm)

4.3.2 Effect of organic concentration

As the loading capacity (and extraction coefficient) of an organic phase varies with the solvent concentration it is important to study this effect. With mixed solvents it is also important to study the effect of their relative concentrations on the efficiency of extraction. For these reasons data was collected to construct $\log E$ vs $\log [\text{Organic}]$ curves¹⁵⁷ (see later) and also to construct continuous variation curves¹⁵⁸ with mixed solvents. In addition data was obtained to give qualitative information about relative loading capacity from equilibrium plots of $[\text{B}]_{\text{org}}$ against $[\text{B}]_{\text{aq}}$.

Experimental

Experiments were carried out as in 4.3.1 except that the contact time was constant (30 minutes) and the concentrations of the single solvents (CTMP or EHD) were varied in the range 0.01 - 1.0 M (pH 5.4/8, 9.1/5) and of mixed solvents (CTMP plus EHD) in the range 0.0 - 0.5 M CTMP, 0.5 - 0.0 M EHD (Total 0.5 M, pH 5.6/8, 8.0/2, 9.0/4). Results are given in Figs. 4.10 and 4.11.

A further series of experiments was carried out at two pH's (5.0/5 and 8.9/9.4) in which the only variable was the phase ratio (in the range 1 : 10 - 10 : 1; aqueous : organic). It proved to be impracticable to study ratio's outside this range. Results are given in Fig. 4.12.

4.3.3 Effect of sodium, calcium, magnesium and chloride ions

A variety of dissolved ions will normally coexist with borates in natural or industrial leach solutions and all may have an effect upon extraction. The most important ions are Na^+ , Ca^{2+} , Mg^{2+} and Cl^- , and

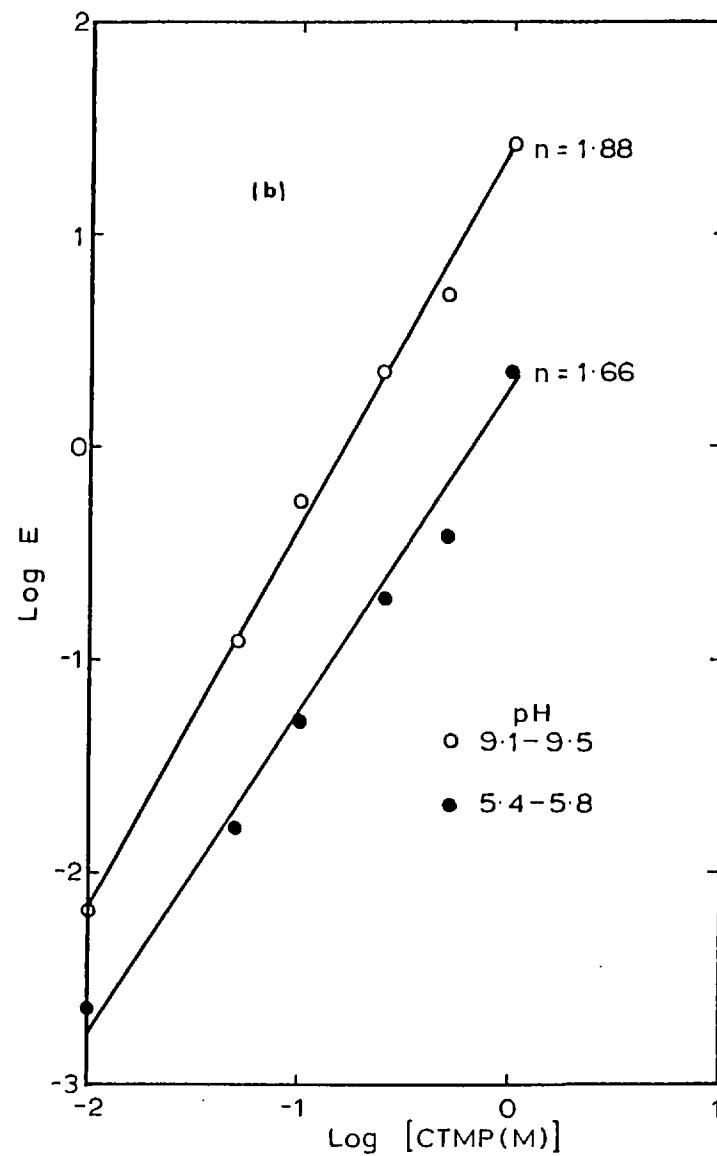
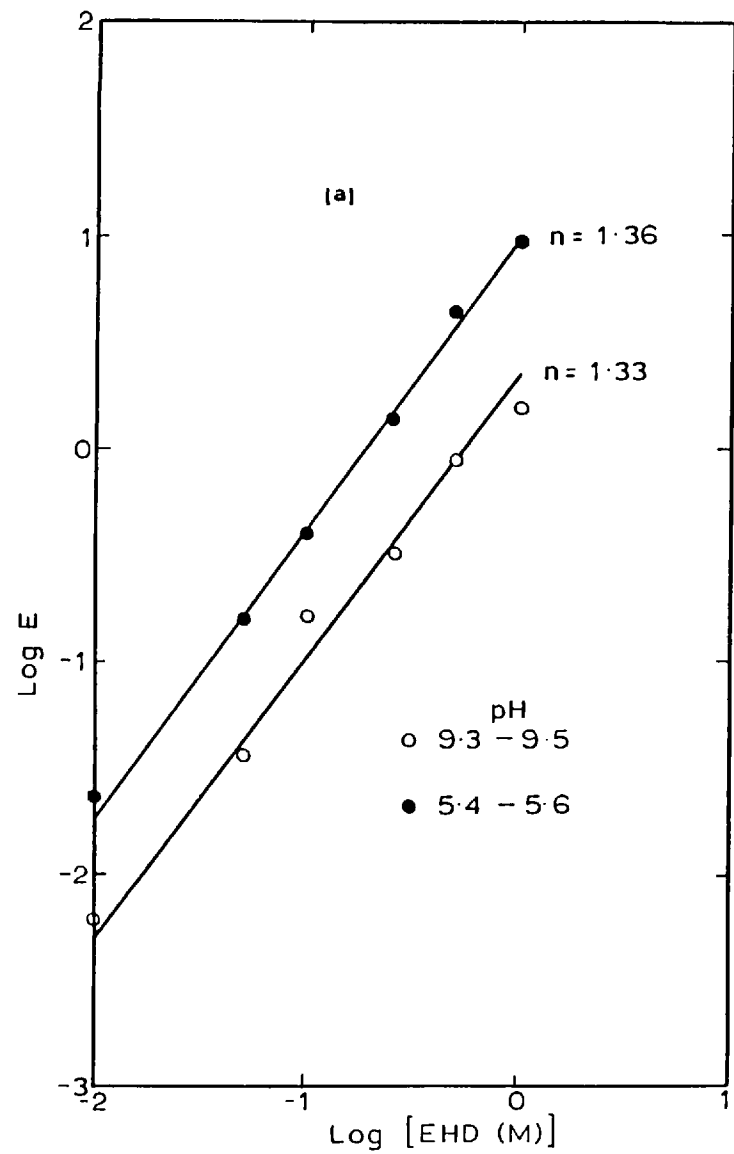


Fig. 4.10 Effect of organic concentration (EHD(a) and CTMP(b) on extraction of boron (500 ppm).

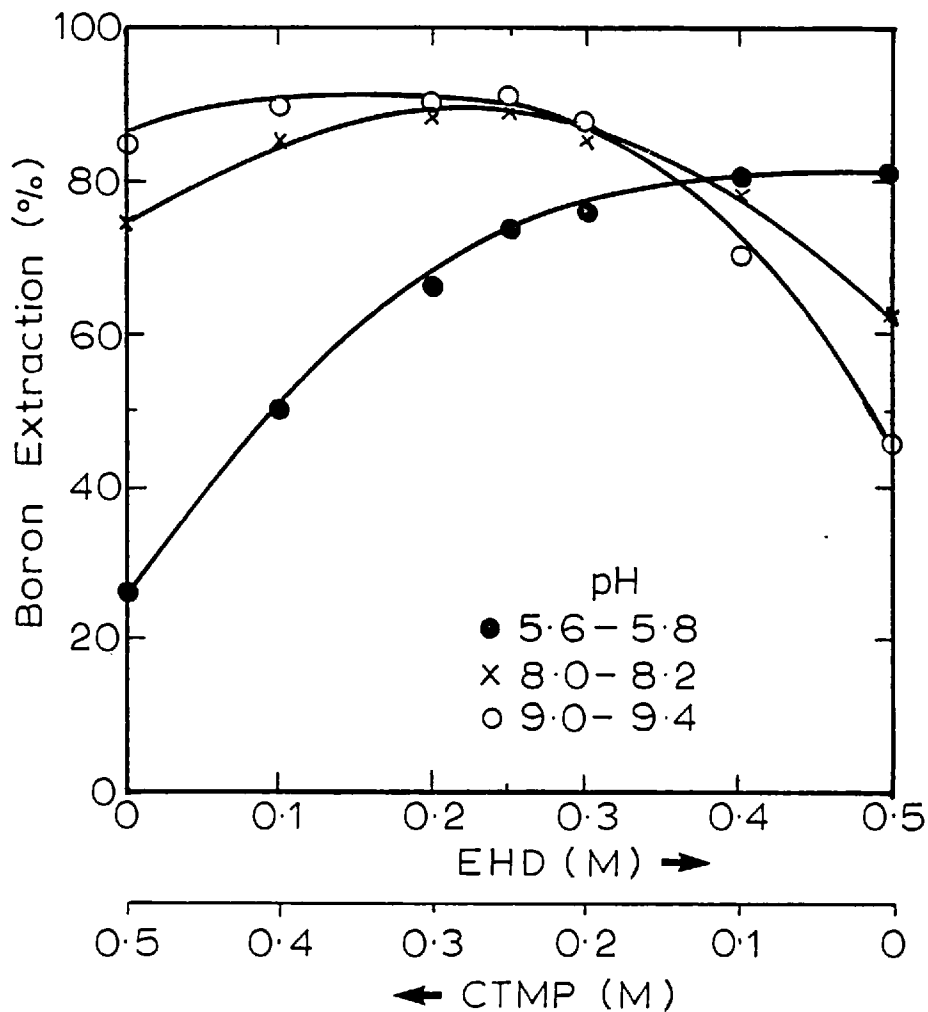


Fig. 4.11 Extraction of boron (500 ppm) with CTMP/EHD mixtures.

the effects of these are considered here. The carbonate ion is also important but is less prominent generally than Ca^{2+} and cannot coexist in solution with this cation at significant concentrations. The extraction of borates, Na^+ , Ca^{2+} , Mg^{2+} and Cl^- singly and in various admixtures into EHD, CTMP and a 1 : 1 mixture of the two was investigated, and reported as curves of % extraction vs equilibrium pH.

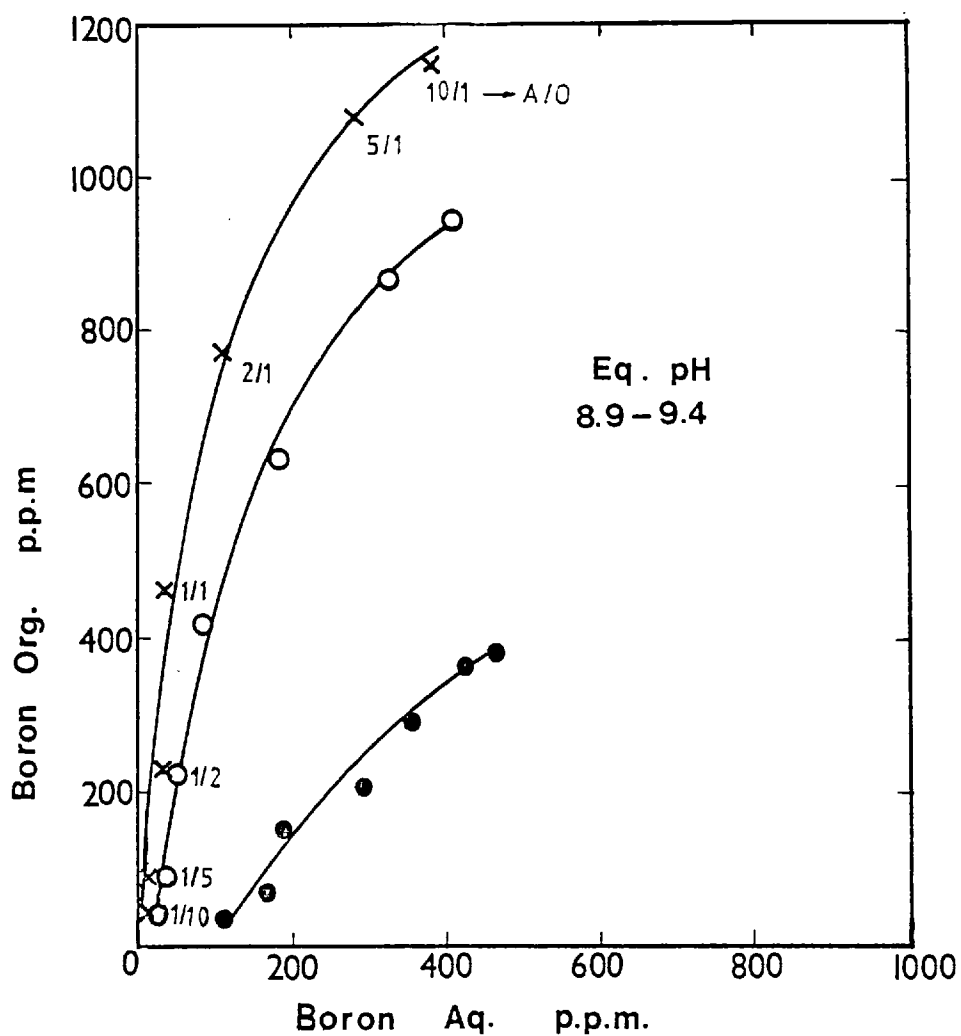
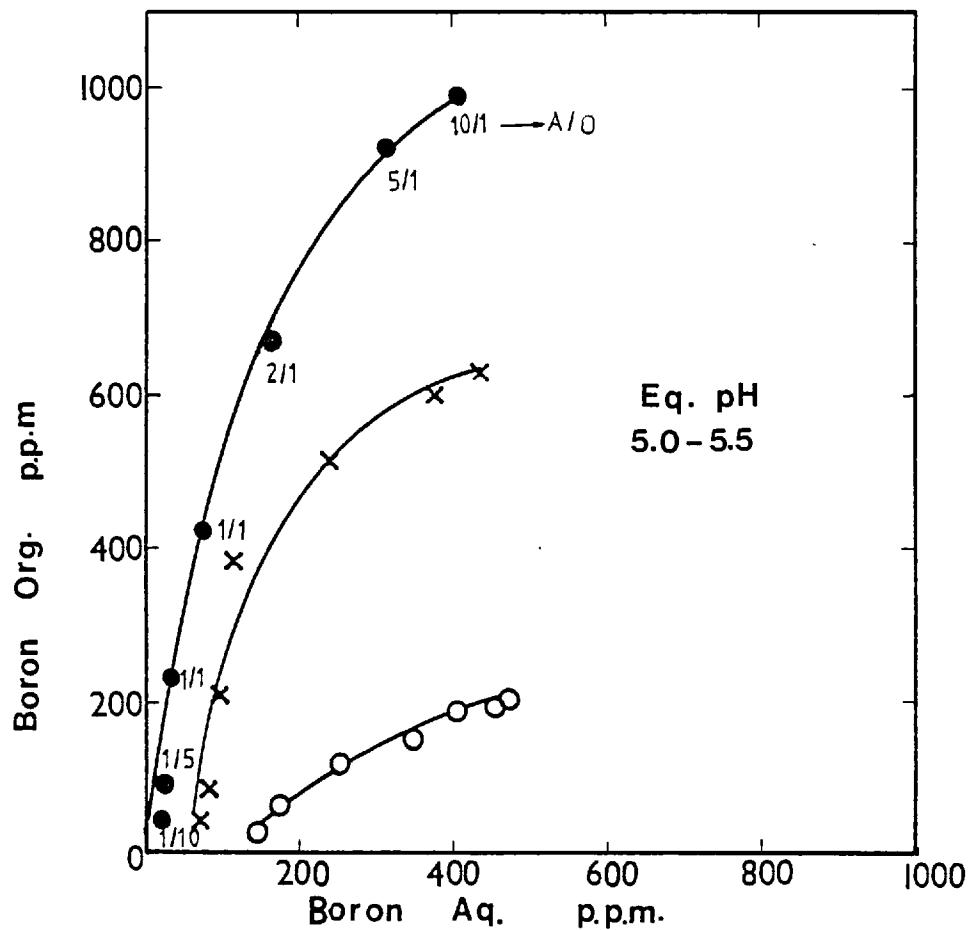


Fig. 4.12. Equilibrium curves for extraction of boron (500 ppm) with EHD (●), CTMP (○) and CTMP/EHD (x).

Experimental

Three types of experimental series were undertaken in essentially the same manner as in previous sections of shake-flask runs: (1) single metal ions or chloride ions were equilibrated separately with the three chosen organic phases at six values between pH 2-11 in the absence of any boron, (2) as in (1) except that the aqueous solution started 0.0463 M in boron, and (3) as in (2) except that all ions were mixed together. In order to avoid confusion of results adjustment of pH in alkaline medium was made using 0.1 M potassium hydroxide. It was assumed that the other ions would react and extract in preference to K^+ . Results are shown in Figs. 4.13 and 4.14 and in Tables 4.3 and 4.4

4.4. Discussion

This discussion will consider firstly the performance of apparatus under the conditions employed, secondly a simple summary of extraction thermodynamics, and thirdly the results of experiments carried out with homogeneous (clear) phases. The general choice of conditions has already received consideration earlier in the chapter. Thus, the work was restricted to (1) solvent extraction of boron and Ca^{2+} , Na^+ , Mg^{2+} and Cl^- ions singly and in admixture (2) the use of a laboratory mixer-settler, shake flasks and a laboratory pulse column and (3) the solvents EHD, CTMP and TBC in petroleum spirit. In fact, for reasons which will become evident, neither the mixer-settler nor the TBC were put to extensive use.

During the construction of the mixer-settler (Fig. 4.4) great care was taken to provide a design in which experimental physical

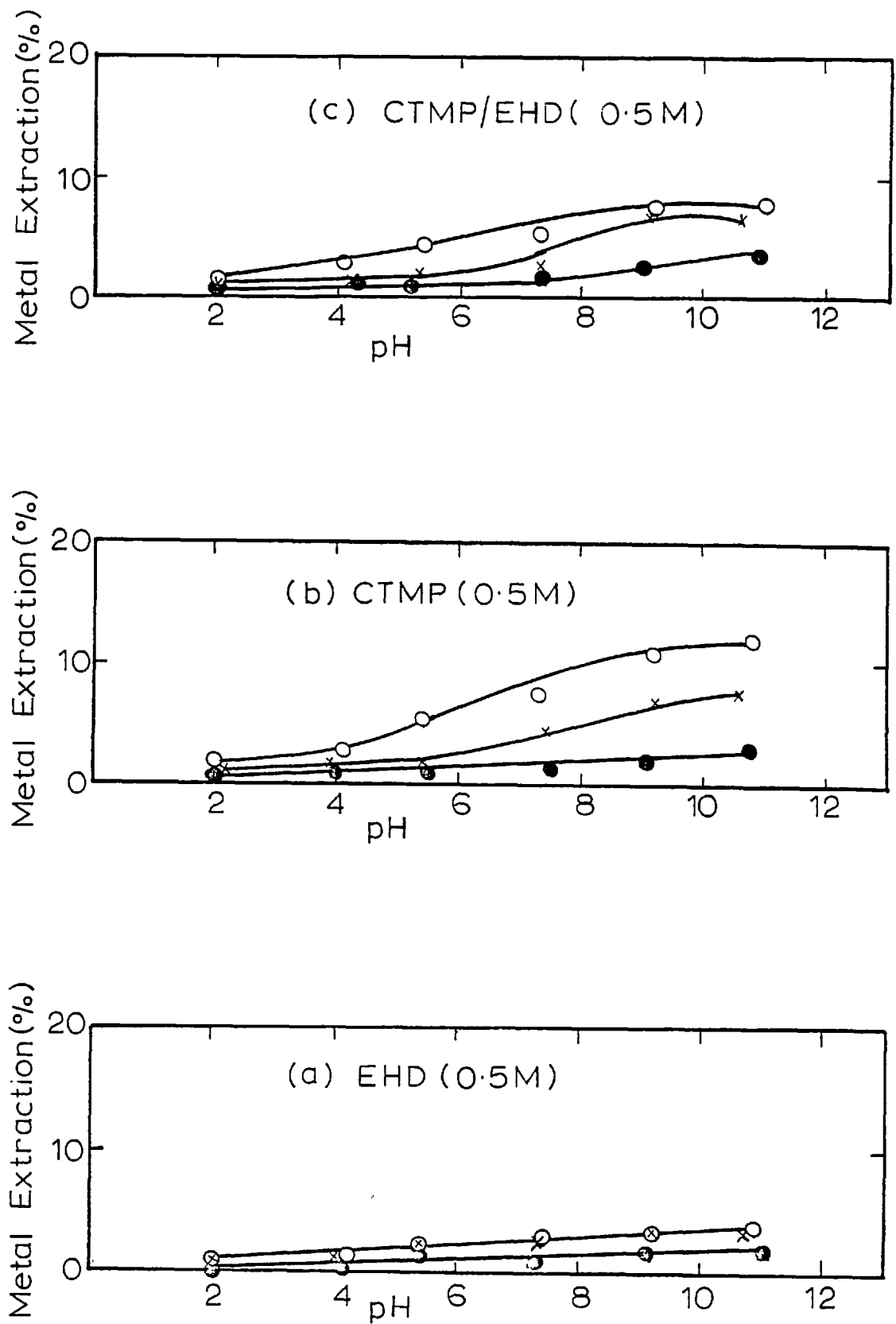


Fig. 4.13. Extraction of Na (●), Ca (○) and Mg (x) all at 500 ppm with EHD (a), CTMP (b) and CTMP/EHD (c)

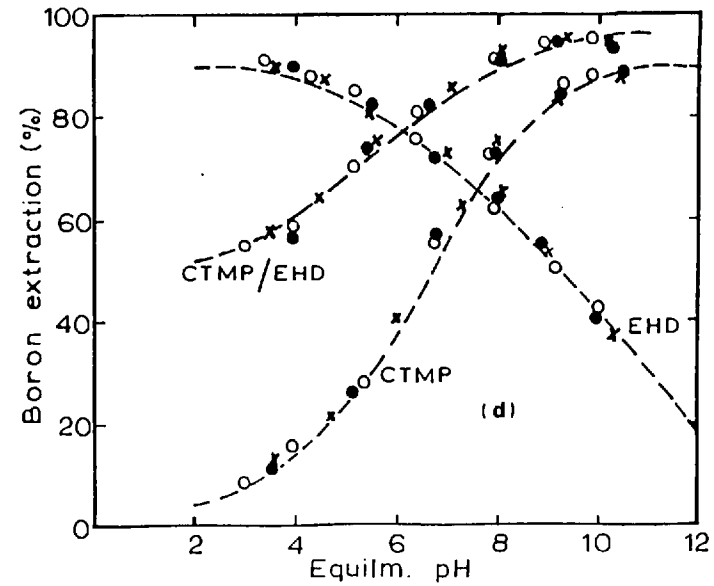
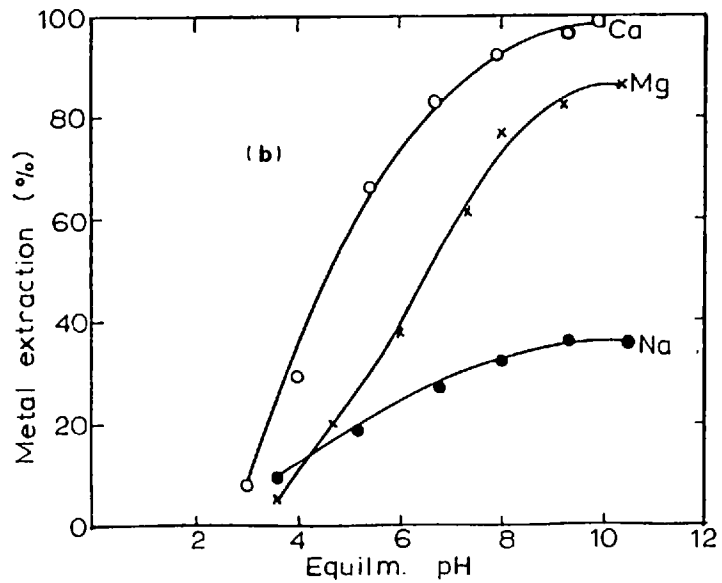
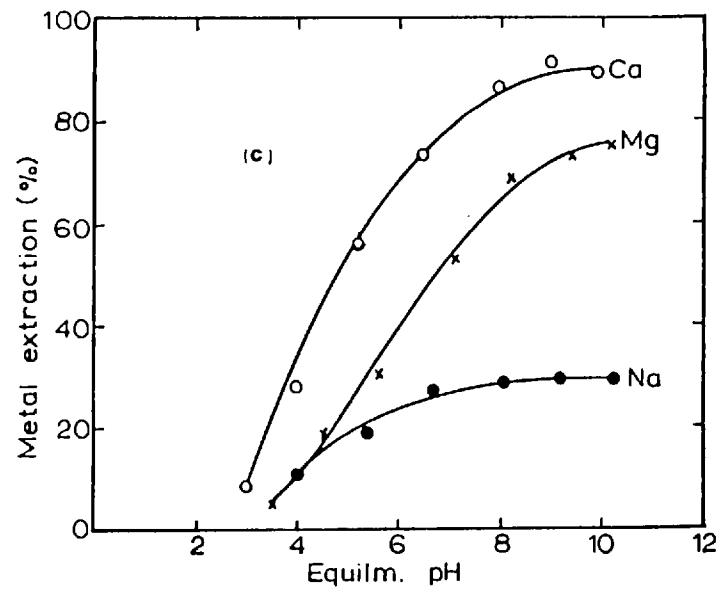
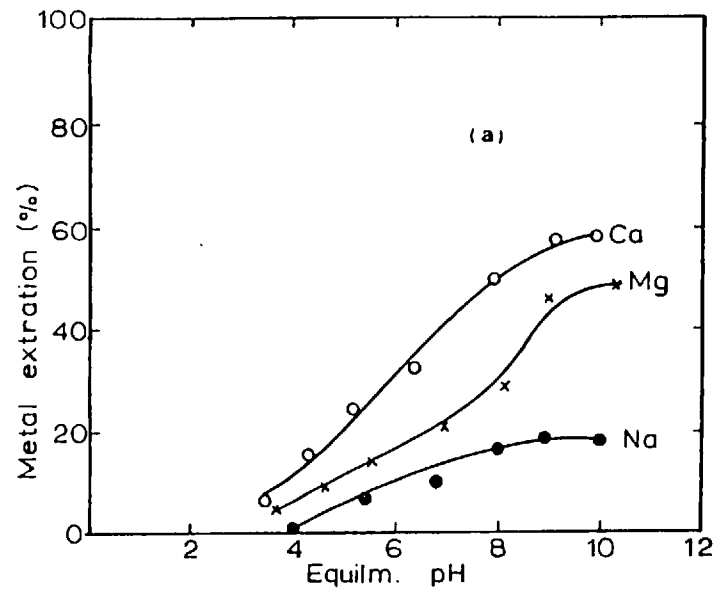


Fig. 4.14 Extraction of Na, Ca and Mg (all at 500 ppm) with EHD (a), CTMP (b) and CTMP/EHD (c), in the presence of boron (500 ppm), d: the effect of these ions on extraction of boron.

TABLE 4.3. EXTRACTION OF CHLORIDE IONS (aqueous to organic ratio 1 : 1, 500 p.p.m. Ca, 884.5 p.p.m. Cl, 500 p.p.m. B and organic concentration of 0.5 M in petroleum spirit)

Organic solvent	Eq. pH	Extraction/%				
		Boron not present		Boron present		
		Ca ²⁺	Cl ⁻	Ca ²⁺	Cl ⁻	(B)
EHD	3.4 - 3.8	1.0	1.1	6.5	1.6	90.6
	5.3 - 5.5	2.3	1.2	25.0	1.7	83.1
	7.8 - 7.9	3.1	1.5	47.0	1.4	63.8
	9.2 - 9.4	4.2	2.3	58.5	2.2	49.0
	10.0 - 10.3	4.4	2.6	57.5	2.4	41.3
CTMP	3.0 - 3.4	2.0	2.1	9.0	1.6	15.3
	5.2 - 5.3	5.1	2.2	62.5	2.1	29.7
	8.0 - 8.1	8.6	4.5	91.0	2.4	71.0
	9.1 - 9.3	11.6	5.7	95.0	3.8	84.2
	10.3 - 10.5	13.0	6.3	97.5	4.2	86.5
CTMP/EHD	3.2 - 3.5	2.3	2.5	10.0	2.3	52.1
	5.1 - 5.5	4.2	2.1	55.0	1.7	72.0
	7.9 - 8.2	6.5	3.0	85.0	1.7	88.1
	9.0 - 9.1	8.5	4.2	90.5	2.1	92.6
	10.2 - 10.3	9.1	4.3	90.0	2.9	94.0

TABLE 4.4. EXTRACTION WITH COMPLETE MIXTURES (aqueous to organic ratio 1 : 1, Na, Ca, Mg and Boron all at 500 p.p.m. and Cl, 3113.5 p.p.m. and organic concentration of 0.5 M in petroleum spirit)

Organic solvent	Eq. pH	Extraction/%				
		Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	(B)
EHD	5.3	3.0	3.0	19.0	-	81.3
	9.1	6.0	27.8	17.5	-	61.0
CTMP	5.3	8.0	26.0	16.5	-	33.6
	9.0	10.0	87.0	13.0	4.3	82.1
CTMP/EHD	5.2	7.0	19.0	2.5	-	76.2
	9.2	8.0	83.0	20.5	2.0	94.1

conditions-temperature, mixing rate, aliquot addition, contact time, pH, evaporation rate and sampling - could be closely reproduced. Quite sophisticated glass-blowing was required but the resulting equipment operated satisfactorily, except that it was necessarily tedious to use for large numbers of experiments. A full run required 2-3 hours for completion. It is much more convenient (though presumably less reliable) to use ordinary shake flasks for which a number of results (about eight) can be obtained in the same time. A comparison of the two methods resulted in Fig. 4.6, from which it is evident that in practice there is little difference in equipment reliability: the spread of results about the 'best curve' is quite large in both cases. A relatively large common error

appears to be operating which swamps any advantage to be gained by use of the more closely controlled mixer-settler equipment. This error can be traced to the critical effect of pH (which cannot generally be adjusted to better than ± 0.5 unit) and to the difficulty in assaying the organic phases directly (a reliable method of assaying the organic phases could not be found and the boron content had to be determined by means of mass balance calculations). Despite the scatter, the results were still meaningful - for instance Fig. 4.6 could become part of a viable McCabe-Thiele diagram¹⁵⁹ - and it became clear that they were best obtained by use of the faster shake-flask technique. The mixer-settler would be more suitable for use at elevated temperatures, but in boron extraction there is little to be gained by temperature change¹²⁶.

The pulse column had the one distinct advantage of being relatively efficient in the extraction of pulps^{114, 152} and its introduction in this chapter had the purpose of describing the apparatus and comparing its operation with that of shake flasks using clear solutions. At the outset, the column was a copy of that of Ritcey¹⁵² but this was found to be unsatisfactory under our operating conditions. Thus, it was found to be necessary to alter the configurations of the pulse inlet and aqueous feed inlet to give vertical applications (together with more closely controlled flow-rates) before an efficient pulsing and mixing action could be obtained. With horizontal or inclined application the pulse was dissipated both upwards and downwards in the column leading to poorer phase contact and contamination of the aqueous raffinate with entrained organic - to further assist the pulsing action the bottom three disks were provided with a larger hole (7 mm diameter) and placed between the level of the pulse

inlet and that of the organic feed inlet. Figure 4.15 gives a self-explanatory indication of the mode of operation of this modification. The majority of ancilliary equipment was specifically tailored to the modified column, the most critical factor being the precise control of flow rates. It was, for instance, found to be essential to meter the aqueous feed both on inletting and outletting although the organic inlet operated satisfactorily merely by overflow.



Fig. 4.15 Photograph showing the operation of the column under modified conditions (the arrows show the position of the 7 mm holes).

In order to optimize the working of the column, five runs were undertaken with conditions varied according to the data in Table 4.2. The alteration of parameters was not comprehensive but nevertheless gave useful insight into the details of phase contact. Thus, it could be seen that % extraction invariably increased with the duration of steady pumping up to the point at which a steady state was achieved, and the extraction at this point varied markedly with the setting of other parameters. From columns (1) and (2) in the Table a decrease in flow rate increased the % extraction by increasing the effective phase contact time, other things being equal. For steady flow rates (columns 2 - 5) of aqueous and organic the % extraction increased by (a) decreasing the disk spacing, (b) making the pulses sharper and (c) decreasing the pulse stroke-length. In each of these cases the increased extraction was presumably due to increased surface area of contact and/or increased efficiency of phase mixing. The final conditions (which were used for all subsequent experiments) could not be improved to give extractions identical to the equilibrium situation achieved in corresponding shake flask experiments (about 82% with EHD) but the difference (2 - 5%) was generally acceptable in the light of overall experimental error. The comparison is illustrated in a self-evident fashion in Fig. 4.7.

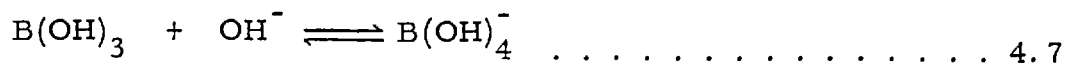
During the course of preliminary solvent extraction experiments use was made of TBC as a solvent and of kerosene as a diluent. TBC is an efficient boron extractant which has been recommended for use under acidic conditions¹²⁷ (pH 5) and is representative of one group of extractants (1, 2 aromatic diols). Boron-containing brines are commonly alkaline (pH 9) and a first prerequisite of any solvent for boron should be stability under these conditions. TBC was acceptably stable below pH 7 but rapidly darkened

in kerosene solution when exposed to light at pH 9. At pH 11 the darkening occurred in 30 seconds. No doubt this decomposition could be prevented by working in the absence of light and/or oxygen but such a course would not be commercially attractive and use of the solvent was discontinued. The use of kerosene was also stopped when it was found that similar results could be obtained with the much 'purer' analogue: AR petroleum spirit. It was assumed that the results would nevertheless apply in a general way to kerosene solvent extraction on a larger scale.

The main bulk of the experimental work with shake flasks was concerned with determining the relative extractabilities of ions and molecules likely to be found in natural boron brines. As can be seen from Fig. 4.8 the rate of boron extraction is quite rapid regardless of the pH and solvent system. The observed order, however is EHD (5 minutes) > CTMP (10 minutes) > EHD/CTMP (15 minutes). These differences have not been investigated in detail as all reactions are sufficiently fast, and for all further experiments a contact time of 0.5 hour could safely be used. However it has been noted previously¹⁶⁰ that mixed ligand systems can cause slow transfer perhaps as a result of the lower individual concentrations available to form a mixed ligand complex, steric inhibition, or adsorption at the phase interface.

The effect of pH is illustrated in Fig. 4.9 in which the basic difference between the extraction properties of EHD and CTMP becomes clear. The former solvent is most efficient at low pH (about 2) and the latter at high pH (about 11 - 12). In the experimental work it was observed that for EHD there was a constant increase in pH on approach to equilibrium while the reverse was the case for CTMP. Although the

equilibria involved are probably complex (equations 4.1 - 4.6) these observations are consistent with the reaction 4.6 being predominant for EHD and reactions 4.3 and/or 4.4 for CTMP. In these deductions equation 4.7 is important because the species involved coexist in variable concentrations dependent upon pH.



If it be assumed that equation 4.5 is operative for EHD extraction then with the usual notation

$$K = \frac{[\text{B(O}_2\text{R)(OH)}]}{[\text{B(OH)}_3] [\text{R(OH)}_2]}$$

from which

$$\log E = \log [\text{R(OH)}_2] - \log K \quad \dots \dots \dots 4.8.$$

where E is the extraction coefficient. A plot of $\log E$ vs $\log [\text{R(OH)}_2]$ should then be a straight line of slope 1. Figure 4.11(a) indicates that this is close to being the case. If on the other hand it be assumed that equation 4.4 is operative for CTMP extraction then

$$K = \frac{[\text{B(O}_2\text{R)}_2^-]}{[\text{B(OH)}_4^-] [\text{R(OH)}_2]^2}$$

from which

$$\text{Log } E = 2 \log [\text{R(OH)}_2] - \log K \quad \dots \dots \dots 4.9$$

A plot of $\log E$ vs $\log [\text{R(OH)}_2]$ in this case gives a straight line of slope 2. Figure 4.11(b) indicates that this is also close to being the case and particularly so at higher pH values where the predominance of the species B(OH)_4^- is greater.

For the mixed solvents the pH effect is much smaller (as might

be expected) but interestingly the overall extraction is improved at higher pH's (i. e. in the range 8 - 12) and the behaviour is rather like that of CTMP. There appears to be a small synergistic effect operating which not only leads to improved extraction but also would make pH control easier. The origin of such an effect may be due to the greater stability or solubility of mixed ligand complexes or to the fact that different ligands preferentially interact with different boron species.

The question arises: can the extraction efficiency be improved by use of a different ligand ratio. Figure 4.11 shows the results as continuous variation¹⁵⁸ experiments in which the ratio of CTMP:EHD was varied through the range 0 - 0.5 M CTMP : 0.5 - 0 M EHD. It is clear that the extraction is best at a 1 : 1 ratio at higher pH values and this is quite good evidence for the formation of a complex containing one ligand of each type under these conditions.

Figure 4.12 shows further data to reinforce discussion on the merits of the mixed solvents at high pH and those of EHD at low pH. The relative loading capacity of these solvents is clearly shown by means of the equilibrium curves¹⁵⁷ shown (Figure 4.12).

Referring to Figs. 4.13 and 4.14 it is feasible to assess the extent of extraction(at equilibrium)of borates and metal cations (as chlorides) into EHD, CTMP and the mixed solvents. In the absence of borates (Fig. 4.13) each of the solvent systems will extract a small proportion of dissolved Na^+ , Mg^{2+} and Ca^{2+} cations, presumably as solvated ion pairs, and the order of extraction is generally $\text{CTMP} > \text{CTMP/EHD} > \text{EHD}$ and $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$ (all exhibiting considerable increases with pH). A maximum is achieved with CTMP at pH 11 when about 11% of the calcium is transferred across the interface. These observations are consistent

with the larger bulk shielding effect of CTMP in ion-pair formation and also with its (likely) stronger acidity. However, it would be expected on grounds of simple polarizing power (charge-radius ratio) that Mg^{2+} would extract to a greater extent than Ca^{2+} . The greater hydration energy of the Mg^{2+} ion may account for this reversal.

The same general trends are observable in Fig. 4.14 (a), (b) and (c), which summarises the extractabilities of the same cations in the presence of boron, but the effects are much greater. Thus, nearly 100% of the Ca^{2+} was transferred with CTMP at pH 10 while even EHD caused extraction of about 20% of the Na^+ ions at this pH. On the other hand, as can be seen in Fig. 4.14 (d) the extent of extraction of boron is little affected by the presence of the cations: there is no definite salting-out effect at the concentrations (roughly 0.01 - 0.03 M) considered. These results can be rationalised if it be assumed that any of the species H^+ , Na^+ , Mg^{2+} or Ca^{2+} can act as the counter ions in the formation and extraction of borate-cation complex ion pairs, and that the order of stability of the ion pairs is generally $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$. Further work would be required to elucidate the detailed associations of the species but it is clear that the cations in brines would substantially effect the operation of a solvent extraction circuit.

Table 4.3 shows how chloride acts as an effective counter anion in the absence of boron and is thus extracted with the solvated cation, and how it competes ineffectively with borates when these are present. Thus, with CTMP/ CaCl_2 6.3% Cl^- is extracted while under comparable conditions with added borate 4.2% Cl^- is transferred.

When a complete mixture of cations and the two anions are

extracted it must be expected that the main species transferred will be the borate-calcium ionpair. This expectation was substantiated by experiments with complete mixtures the results of which are summarised in Table 4.4. As an example from the Table with CTMP at pH 9, the proportions of elements extracted were 10.0% Na, 87.0% Ca, 13.0% Mg, 4.3% Cl^- and 82.1% B.

CHAPTER 5
EXTRACTION FROM SLURRIES

5 EXTRACTION FROM SLURRIES

Effluents from borate treatment plants are likely to contain up to 15% of suspended matter (in addition to dissolved contaminants) in the form of finely divided clays, quartz, carbonates and borates. The purpose of this final chapter is to consider ways in which boron can be removed from such slurries by solvent-in-pulp extraction.

5.1 Extraction experiments with synthetic and natural slurries

The solids content of an important type of slurry effluent was given in chapter 2 (Table 2.7) wherein it can be seen that the main solids requiring consideration are clays (montmorillonite, illite and hectorite mainly), carbonates (calcite and dolomite), and borates (inyoite, indurite, etc.) Quartz is also a likely constituent. In order to elucidate the behaviour of several types of solid singly it was decided to carry out pulse column solvent-in-pulp experiments with synthetic slurries containing bentonite/hectorite (representative of the dioctahedral and trioctahedral clay series respectively), calcite/dolomite, and quartz. (For reasons which will become clear precise data for hectorite, calcite and dolomite were not however obtained). Additionally, analogous experiments were carried out with authentic industrial slurry containing these minerals together with borates. Two types of experiments were undertaken: open circuit runs similar to those in section 4.2, and partially closed-circuit experiments in which several extractions of a single volume of aqueous feed were made with fresh volumes of organic feed.

5.1.1 Pulse column experiments in open-circuit

The purpose here was to compare the efficiency of extraction with that achieved (section 4.3.1) in the absence of suspended solids.

Experimental

The column was set up and operated as explained previously (section 4.2) except that the requisite solids were added (at 5% w/v) to the aqueous phase, and both phases were sampled under steady state conditions. Some characteristics of the solids used are given in Table 5.1. The origin of the minerals was: bentonite, calcite and dolomite (Gregory Bottley & Co., London), hectorite (Natural Science Establishment Inc., New York) and quartz (common sample). They were crushed and ground as necessary to give a homogeneous product at -200 # (75 μm). The data in the Table was obtained by use of standard techniques - the Warman International Ltd. SY23 sub-sieve sizer¹⁶¹ (Sydney) for particle size distribution and the BET method¹⁶² for surface area determinations. The method of isolating solids for measurement from the industrial slurry (Kirka Boraks Ltd.) was given earlier (section 2.3.2).

The phases were sampled (50 cm³ of each) after the steady state had been reached and were treated as follows.

Aqueous: solid-liquid separation was achieved by centrifuging and decantation, and assay by acid-base titration of 25 cm³ aliquots (Chapter 3).

Organic: The efficiency of phase separation was estimated from direct turbidimetric measurements (see later).

The equilibrium data obtained are given in Figures 4.7 and 5.1 in comparison with analogous clear solution shake-flask and pulse column

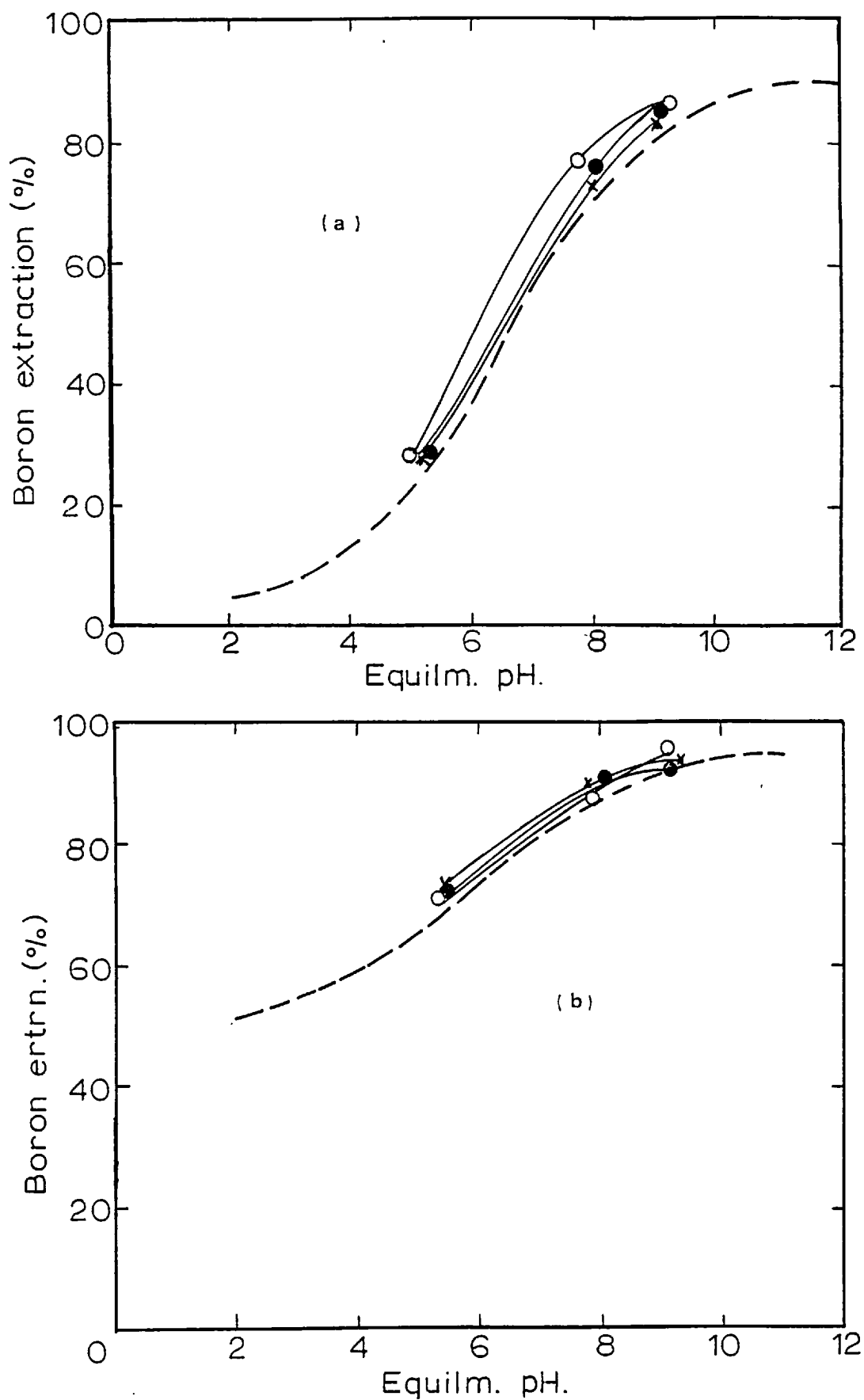


Fig. 5.1 Extraction of boron from slurries (5% solids) with CTMP (a) and CTMP/EHD (b) in sieve-plate-pulse column, clear soln. (●) bentonite slurry (○) and quartz slurry (x) compared with. (---): shake-flask exps. (clear solutions).

TABLE 5.1. SIZE DISTRIBUTION ANALYSIS

size distr. (μm)	bentonite			hectorite			calcite			dolomite			quartz			slurry (Kirka)		
	g	wt %	$\Sigma\text{wt}\%$	g	wt%	$\Sigma\text{wt}\%$	g	wt%	$\Sigma\text{wt}\%$	g	wt%	$\Sigma\text{wt}\%$	g	wt%	$\Sigma\text{wt}\%$	g	wt%	$\Sigma\text{wt}\%$
-75 +40	0.8	3.2	100.0	2.8	11.2	100.0	9.4	18.8	100.0	7.2	14.4	100.0	6.7	13.4	100.0	1.9	7.6	100.0
-40 +30	0.5	2.0	96.8	1.9	7.6	88.8	5.9	11.8	81.2	4.8	9.6	85.6	6.0	12.0	86.6	1.4	5.6	92.4
-30 +20	0.5	2.0	94.8	2.0	8.0	81.2	6.3	12.6	69.4	5.8	11.6	76.0	8.0	16.0	74.6	1.7	6.8	96.8
-20 +15	0.4	1.6	92.8	1.6	6.4	73.2	5.3	10.6	56.8	5.6	11.2	64.4	6.2	12.4	58.6	1.1	4.4	80.0
-15 +10	0.5	2.0	91.2	1.0	4.0	66.8	3.1	6.2	46.2	3.4	6.8	53.2	3.4	6.8	46.2	0.9	3.6	75.6
-10	22.3	89.2	89.2	15.7	62.8	62.8	20.0	40.0	40.0	23.2	46.4	46.4	19.7	39.4	39.4	18.0	72.0	72.0
TOTAL	25.0	100.0		25.0	100.0		50.0	100.0		50.0	100.0		50.0	100.0		25.0	100.0	
surface area m^2g^{-1}	8.1			4.8			1.0			1.9			1.1			6.3		

runs, and turbidimetric results are given in Fig. 5.2.

It was found that calcite and dolomite collected above the aqueous/organic interface and precluded the establishment of quantitative data in these cases. Preliminary experiments in shake flasks indicated that hectorite and bentonite behaved similarly and full experiments were only undertaken with the latter.

5.1.2 Pulse column experiments in partial closed-circuit

The main consideration of this section is the collection of data relating to the reduction of boron content in slurries to an environmentally acceptable level (5 ppm) by runs of repeated solvent extraction.

Experimental

The column was filled and set-up for partial closed-circuit operation as described in section 4.2. The contained approximately 400 cm^3 of aqueous phase was then contacted with organic phase as before over 1.5 hours, before taking 25 cm^3 samples of both phases and stopping the flows. Assay of the aqueous phase was carried out by means of the centrifuging and curcumin techniques (sections 5.1.2 and 3.2.1) and of the solids content in the organic phase by turbidimetry (see later). As 1 cm^3 only of the aqueous phase was required for the assay some 24 cm^3 could be returned to the phase bulk after reconstitution (this avoided substantial reduction of the bulk aqueous volume during succeeding extraction stages). This bulk was adjusted to the starting pH about 7.5 (EHD), 9.4 (CTMP) and 9.2 (CTMP/EHD) from the steady state value of about 8, and replaced in the column with the aid of a funnel. Contacting with the (fresh) organic

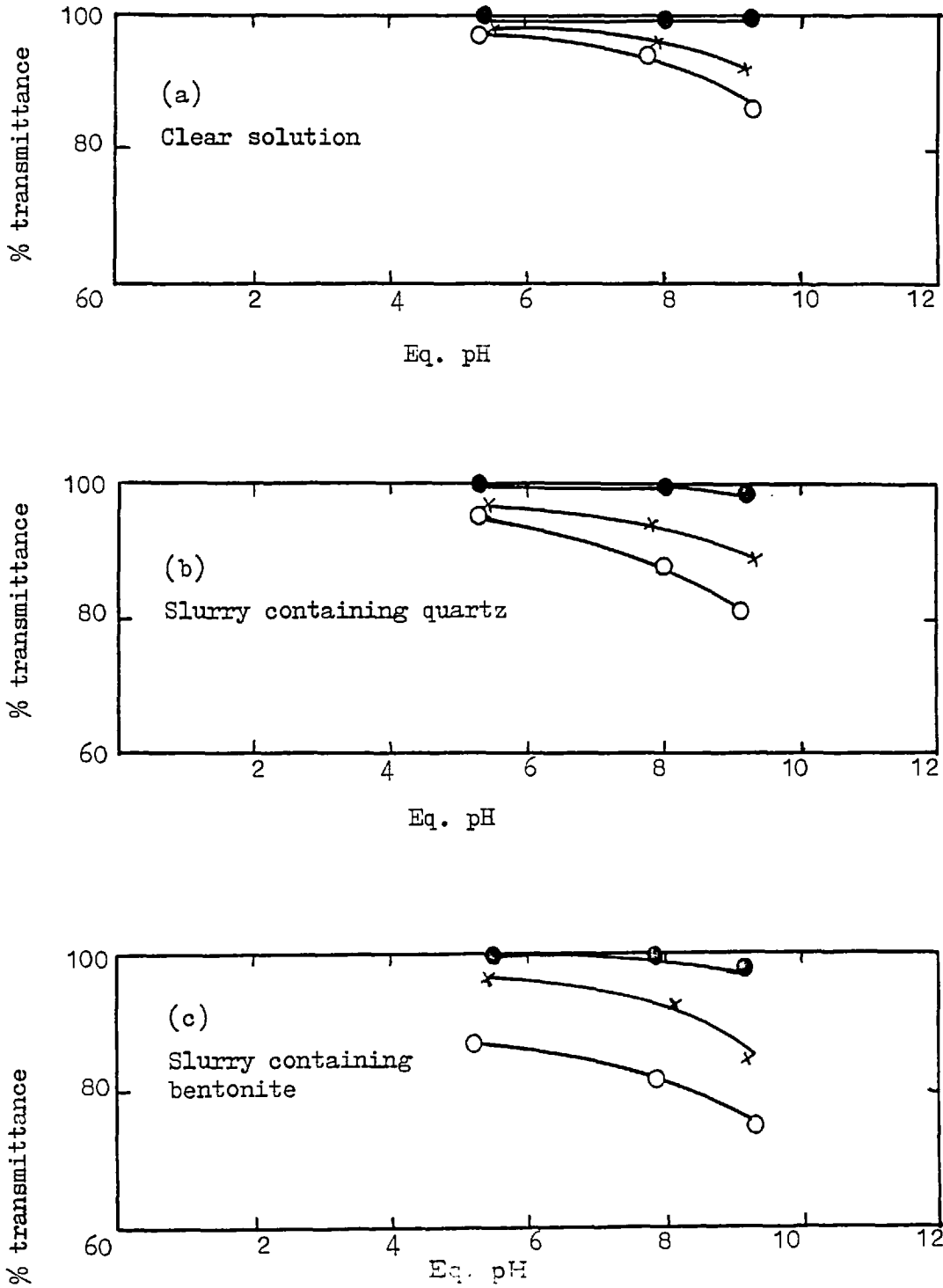


Fig. 5.2 % transmittance of the organic phases (CTMP(o), CTMP/EHD (x) and EHD (●)) resulting from the extraction of boron (500 ppm) using sieve-plate-pulse column in open circuit, (clear solutions (a), quartz slurry (b) and bentonite slurry (c)).

phase was then restarted and the whole procedure repeated the required number of times to achieve an aqueous raffinate containing less than 5 ppm B.

Results are shown for bentonite in Figures 5.3 and 5.4 (a) and for the Kirka slurry in Figures 5.4 (b) and 5.5. Turbidimetric measurements relevant to the latter slurry are given in Fig. 5.6.

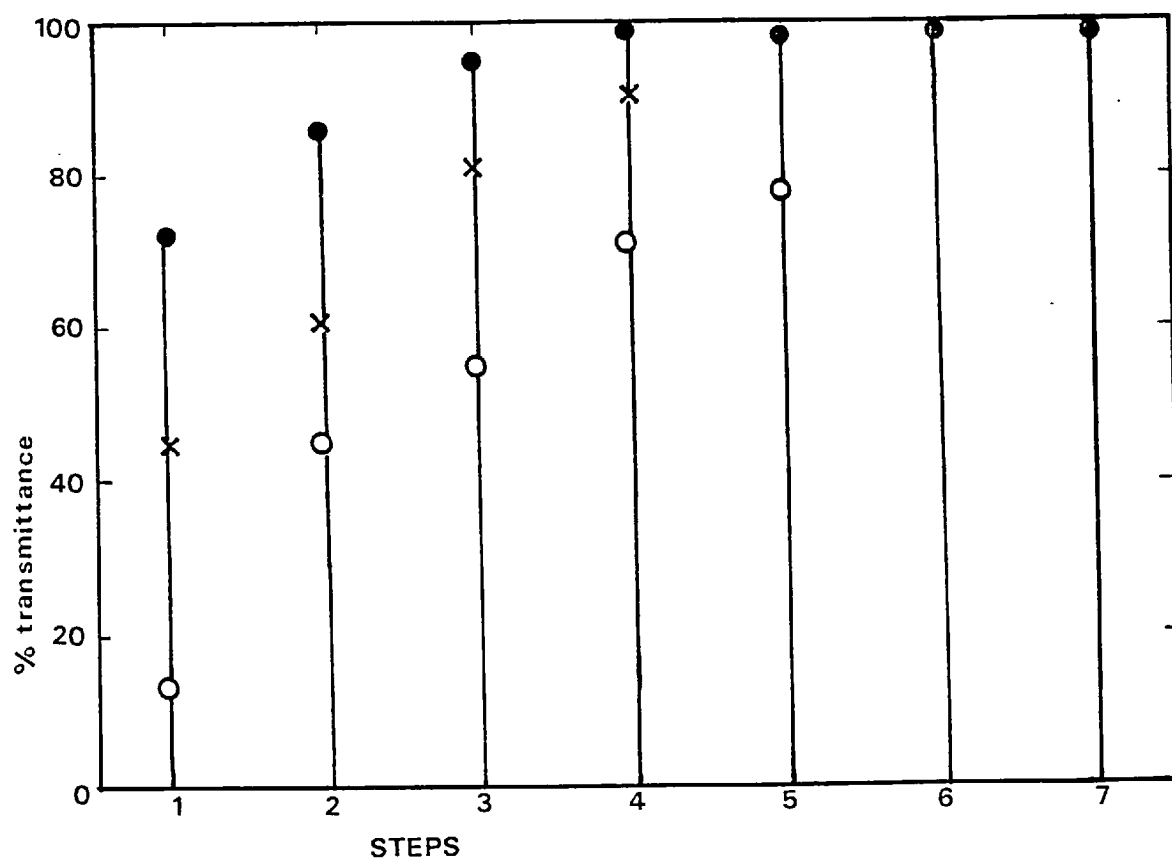


Fig. 5.6 % transmittance of the organic phases (CTMP (o), CTMP/EHD (x) and EHD (●)) in successive extraction of boron (4361.5 ppm) from Kirka slurry using sieve-plate-pulse column

5.2 Investigation of the clarity of the organic phases

A proportion of the aqueous slurry will be dissolved and entrained in the organic phase during extraction. The purpose now is to report

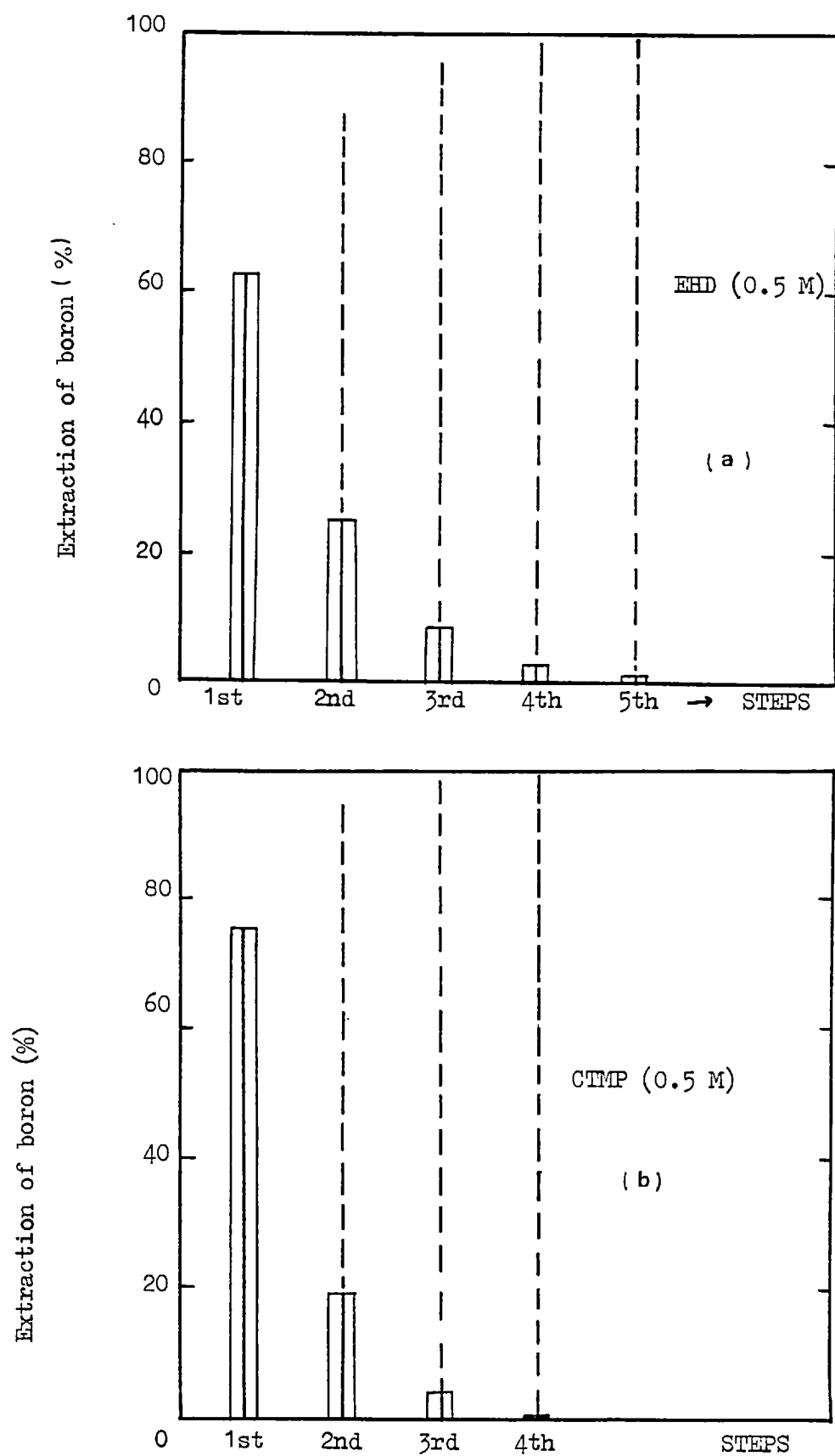


Fig. 5.3 Number of stages needed to reduce boron in solution to below 5 from 500 ppm in successive extraction from bentonite slurry (5% solids) with EHD (a) and CTMP (b) using sieve-plate-pulse column in partial closed-circuit

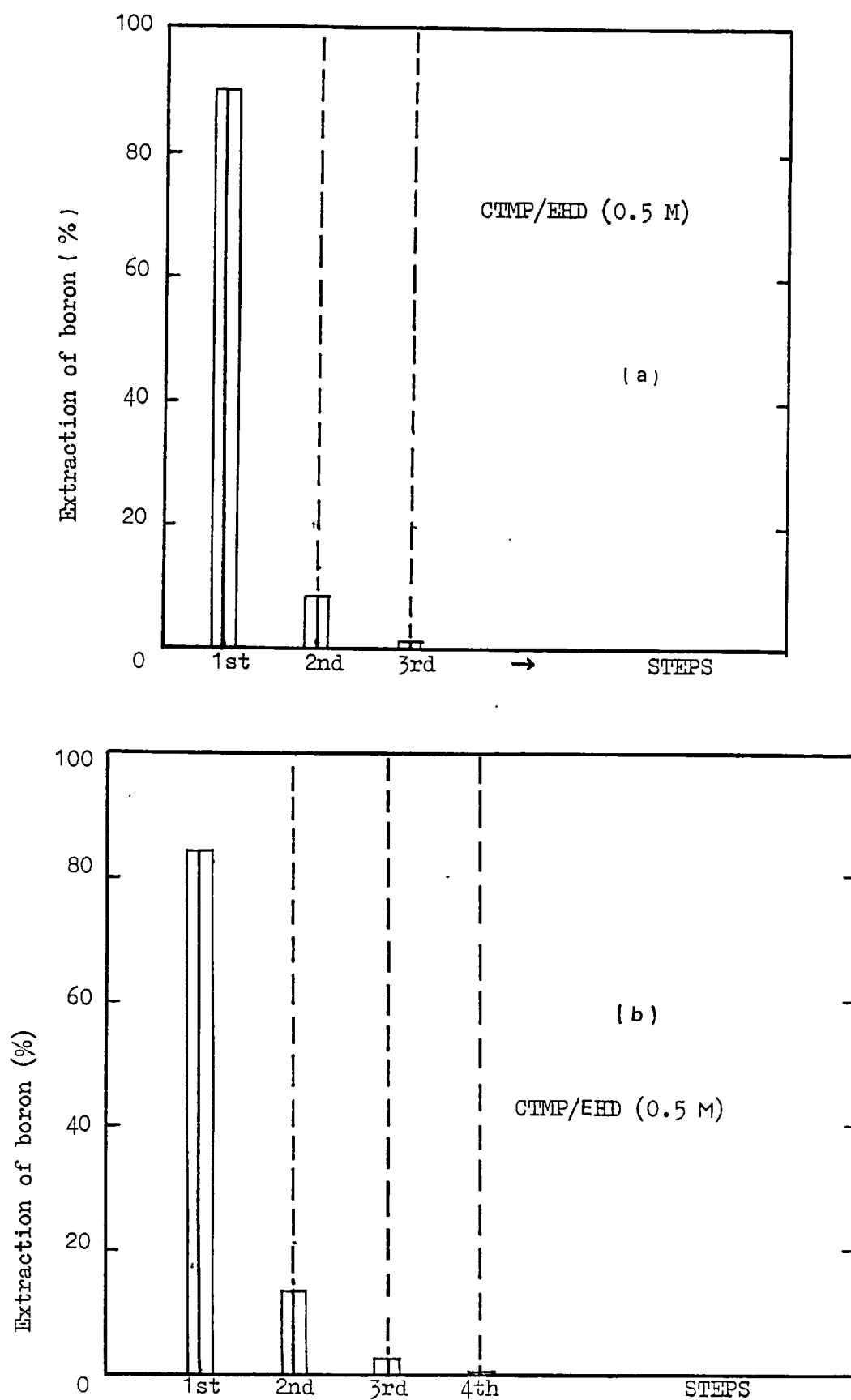


Fig 5.4 Number of stages needed to reduce boron in solution to below 5 ppm from bentonite slurry containing 500 ppm B (a) and Kirka slurry containing 4361.5 ppm (b) with CTMP/EHD (0.5 M) using sieve-plate-pulse column in partial closed circuit

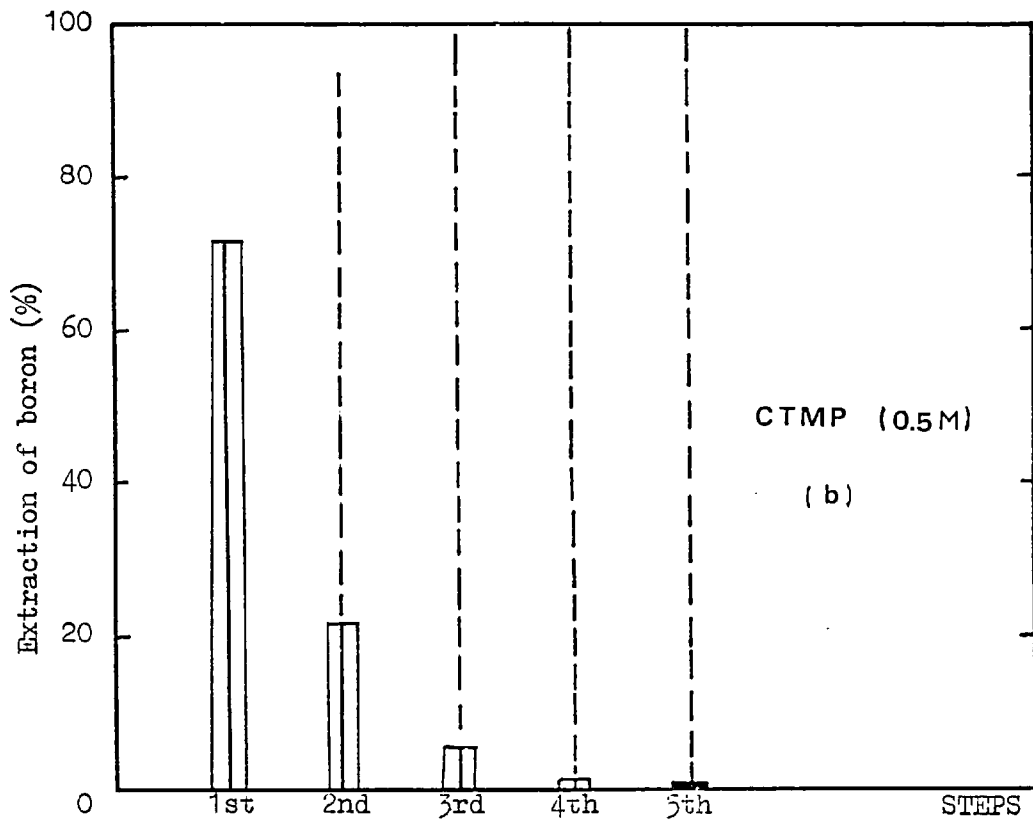
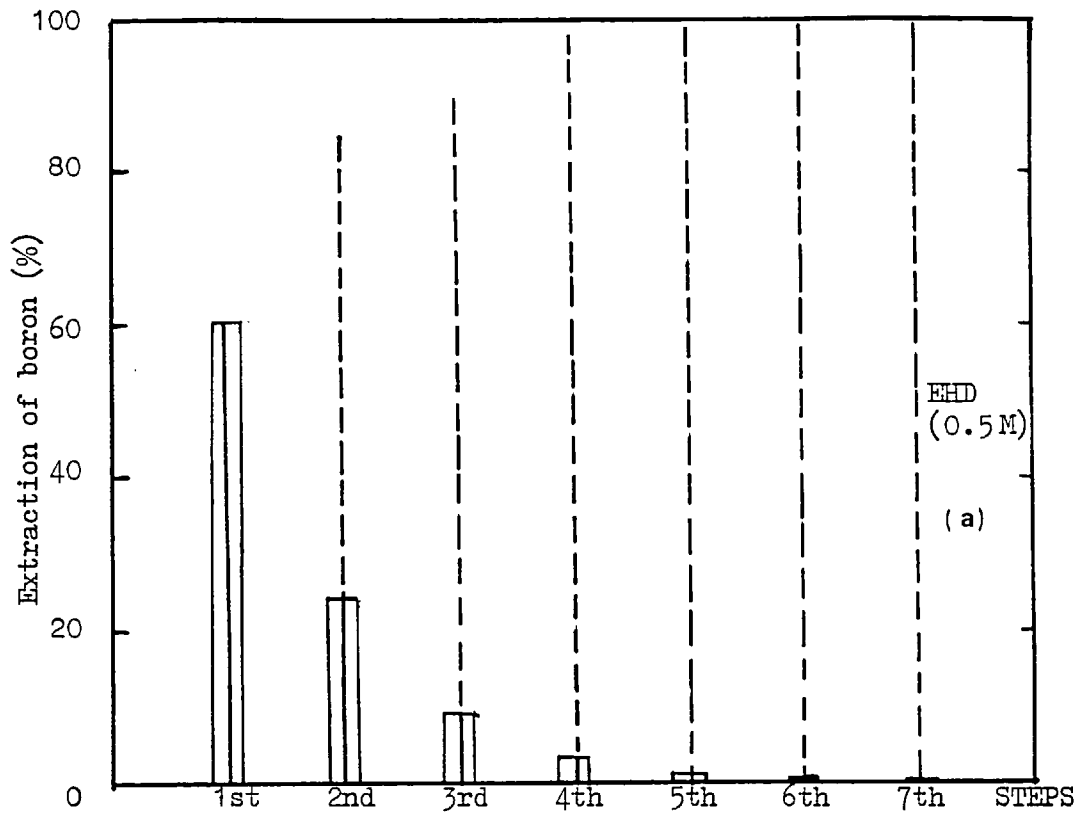


Fig. 5.5 Number of stages needed to reduce boron in solution to below 5 from 4361.5 ppm in successive extraction from Kirka slurry (4.5% solids) with EHD (a) and CTMP (b) using sieve-plate-pulse column in partial closed-circuit.

studies of the entrainment of water and suspended solids in 0.5 M solutions in petroleum spirit of EHD, CTMP and the mixed solvents. Turbidimetry was the main analytical tool employed.

Experimental

The turbidimetric measurements were carried out using an EEL Absorptiometer in conjunction with 1 cm glass cells. Standard suspensions were prepared by mixing 1 g of bentonite or quartz in 100 cm³ of the requisite organic solution (for 1 minute) with aid of a Soniprobe-Dawe Instruments ultrasonic mixer. The suspensions were allowed to stand undisturbed for 15 minutes before decanting a proportion of the stable phase into a 100 cm³ volumetric flask, which was then made to the mark with the corresponding clear organic solution. The residual solids/suspension was filtered, and the solid fraction recovered, dried and weighed; the mass obtained being used to determine by difference the concentration of suspended solids in the volumetric flask. A number of standard suspensions in the range 0-800 gm⁻³ were prepared by suitable dilution. Measurements of turbidity were then made (against clear organic solutions) within 15 minutes according to standard practice¹⁶³. Figures 5.7 and 5.8 give the results obtained plotted as % transmittance against mass of solid (g) per unit volume (m³) suspension.

The figures also contain data on the turbidity caused by suspended water in the organic phases. Water suspensions were prepared by dispersing 0.8 cm³ (the maximum possible for 15 minute stability as determined by trial and error) water in 100 cm³ organic using the Soniprobe mixer as before. In addition Fig. 5.8 contains analogous data obtained for mixed quartz/bentonite/water phases.

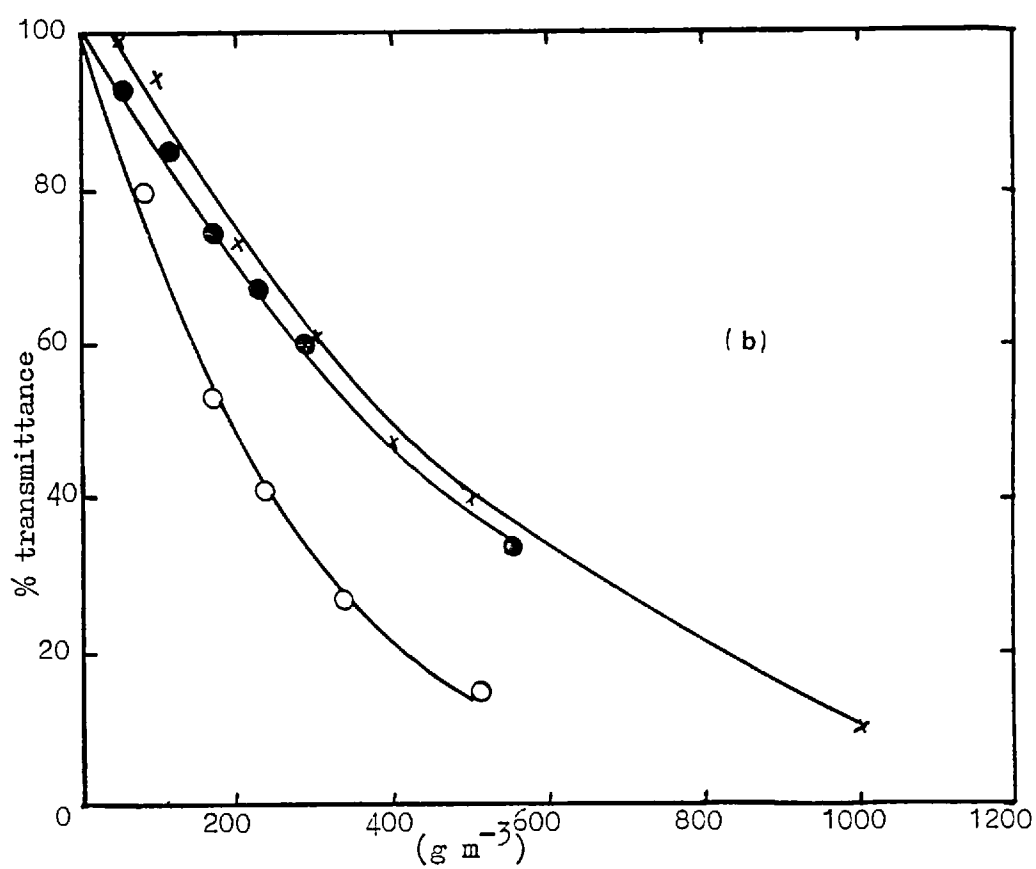
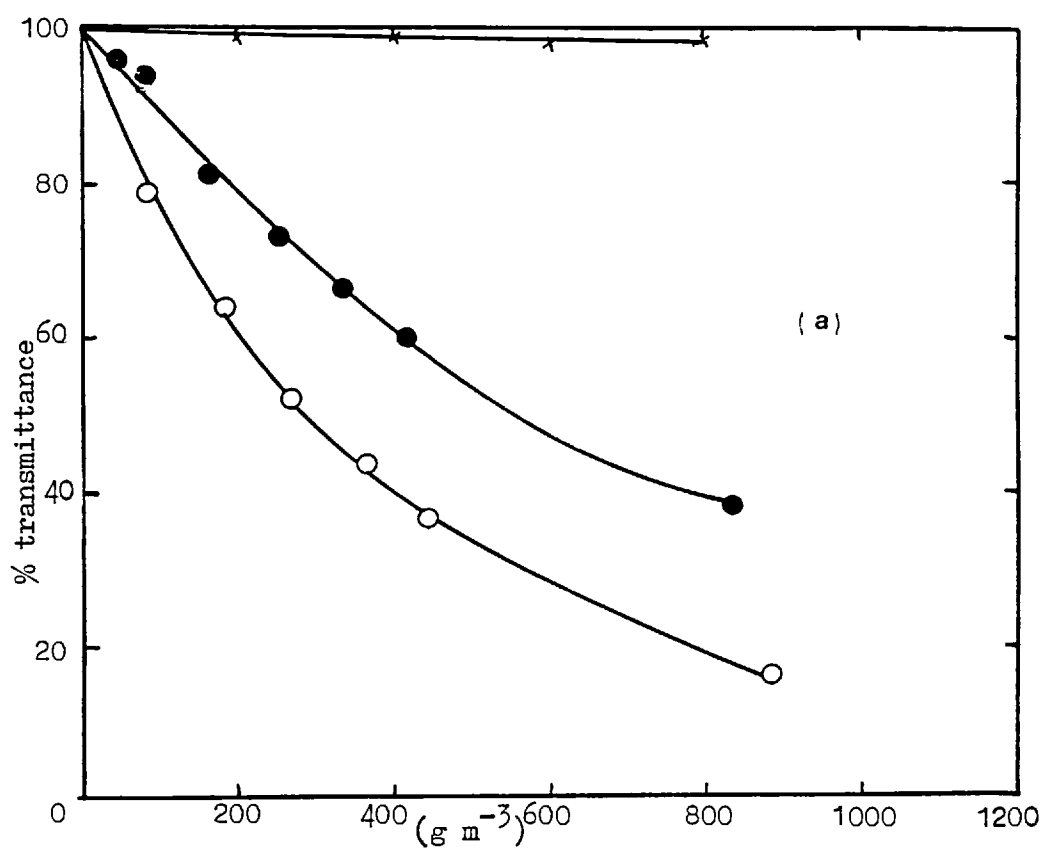


Fig 5.7 % transmittance of EHD 0.5 M (a) and CTMP/EHD 0.5 M (b) in the presence of water (x), bentonite (●) and quartz (○)

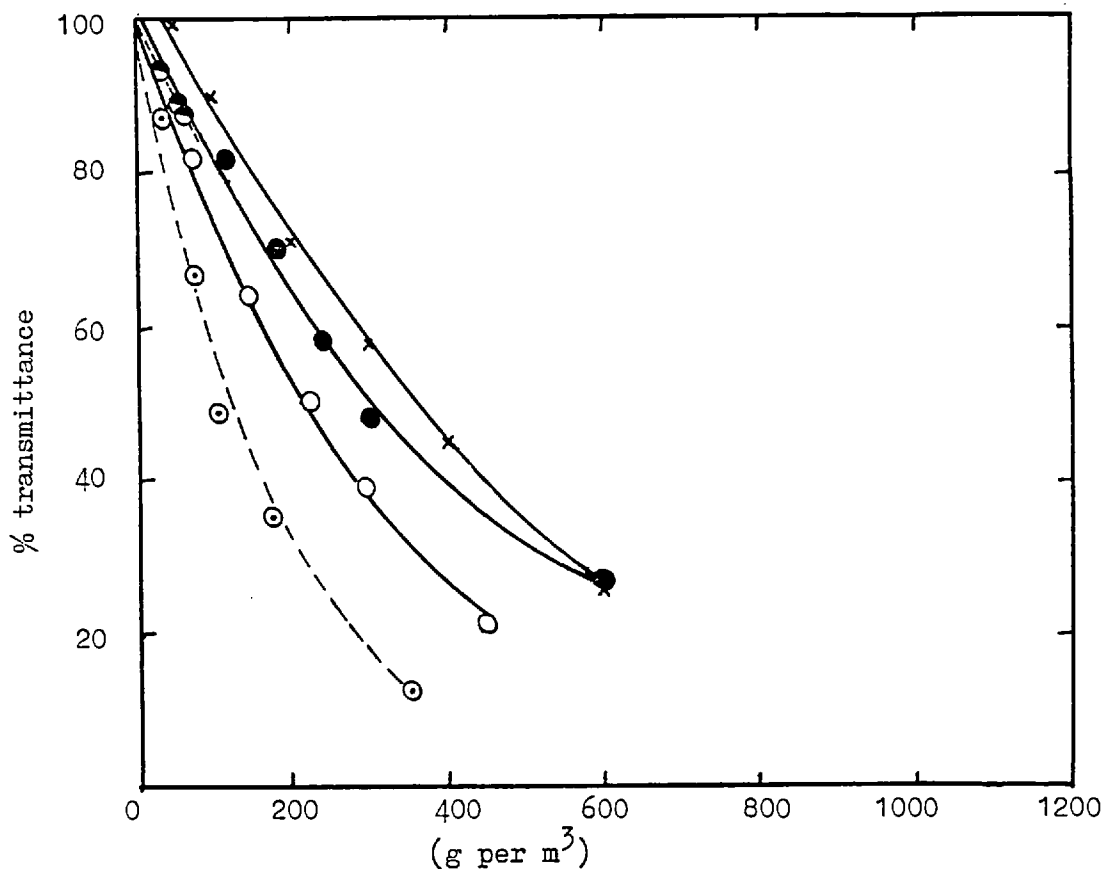


Fig 5.8 % transmittance of CTMP (0.5 M) in the presence of water (x), bentonite (●), quartz (○), quartz-water (⊙) and bentonite-water (⊖)

5.3 Investigation of solvent losses

Losses in the solvent inventory during processing constitute a major factor in solvent extraction technology because not only are the solvents expensive but they are also potential pollutants. The problem is particularly acute in pulp extraction for which three modes of loss need consideration: dissolution in the aqueous phase, adsorption onto suspended particles, and physical entrainment in the pulps and crud formation¹¹⁴. This section deals with estimates of solubility, adsorption on mineral particles and entrainment of CTMP in the aqueous slurry phase. The main analytical tool is UV spectrophotometry.

Experimental

The spectrophotometric experiments on CTMP solubility were substantially as described in Chapter 3. Results relevant to eight pH

values are given in Fig. 5.9.

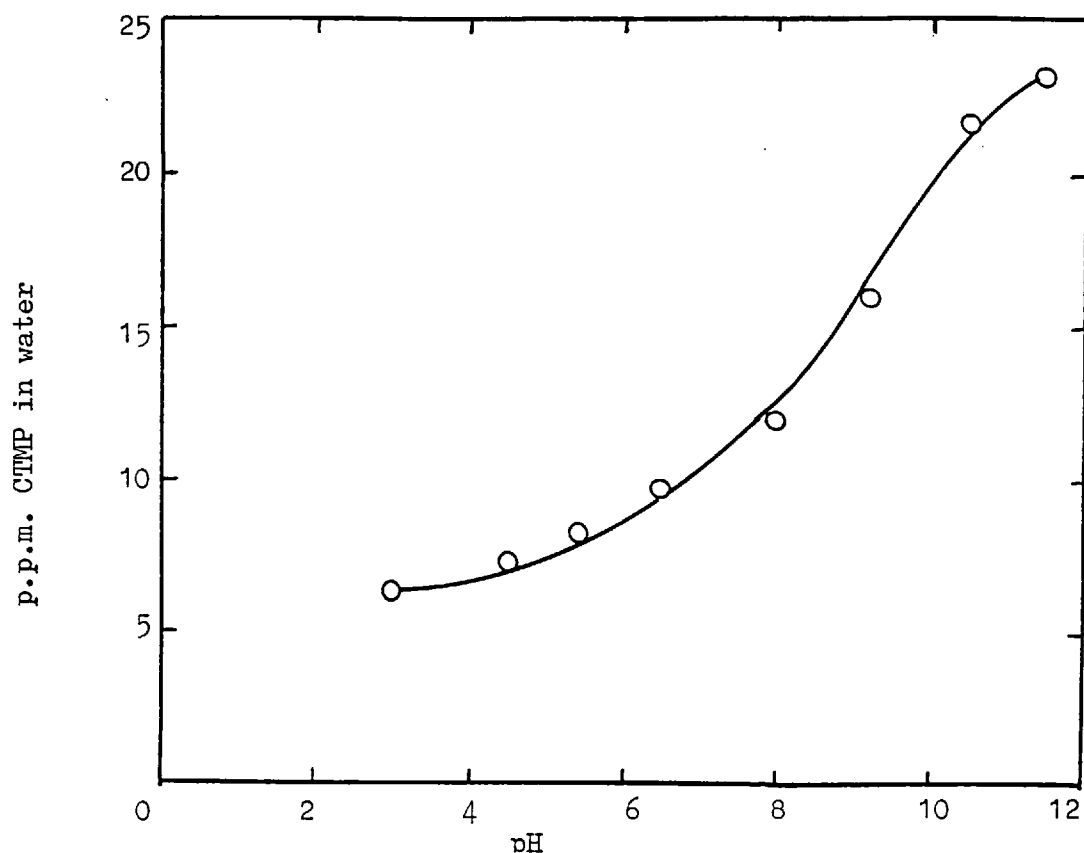


Fig 5 9 Solubility of CTMP in water

Adsorption measurements were conducted as follows: 2.5 g solids (bentonite, hectorite, calcite, dolomite, quartz or natural (Kirka) clay/borate mixtures), 50 cm³ water and 50 cm³ 0.5 M CTMP in petroleum spirit were shaken together for 90 minutes using the Griffin and George flask shaker. The aqueous phase was separated with the aid of a tap-funnel and centrifuged; 5 cm³ petroleum spirit was carefully mixed with the upper part of the supernatant aqueous phase (avoiding disturbance of the sedimented solids) and the combined liquid phases decanted into a tap funnel; and the residual solids were washed with water by centrifuge and dried, the washings being bulked in the tap funnel containing the decanted liquid phases obtained earlier (see below). 0.25 g of the dry solids were leached by vigorous agitation for 5 minutes with pure petroleum spirit

(100 - 120°C); the phases were again separated by centrifuge; and the resulting clear solution assayed for CTMP spectrophotometrically in the normal manner. Results obtained for the mineral phases mentioned at pH values of about 5, 8, 9 and 11 are given in Table 5.2.

TABLE 5.2. ADSORPTION OF CTMP ONTO MINERAL SURFACES
(equilibration time 90 minutes)

Mineral	pH	g CTMP m ⁻³ slurry flow	g CTMP per ton solid
Quartz	5.4	8.5	170.0
	7.8	8.0	160.0
	9.4	8.7	174.0
	11.5	9.0	170.0
Bentonite	5.5	12.0	240.0
	7.7	12.2	244.0
	9.3	11.5	230.0
	11.2	12.0	240.0
Hectorite	5.4	12.7	254.0
	7.9	12.2	244.0
	9.4	13.0	260.0
	11.2	12.7	254.0
Calcite	6.5	80.0	1600.0
	7.8	81.0	1620.0
	9.2	83.5	1670.0
	11.3	81.0	1620.0
Dolomite	6.6	76.0	1520.0
	8.0	77.5	1550.0
	9.1	80.0	1600.0
	11.3	76.0	1520.0
Slurry (Kirka)	9.2	29.5	649.0

Estimates of entrainment were made (for bentonite and the Kirka slurry) using the bulked aqueous phases resulting from the adsorption experiments above. The combined phase (about 25 cm³ aqueous and 5 cm³ organic) were separated in the tap-funnel and the organic layer assayed for CTMP as before. Results obtained were 107 and 110 gm⁻³ for bentonite and Kirka slurry respectively at pH 9.2.

5.4 Discussion and proposals

Solvent-in-pulp extraction can only be successful if a sufficiently sharp separation of the phases is feasible after mixing and, in particular, if the adsorption/entrainment of solvent in the particles, and the transfer of solids into the organic phase or interface are minimal. These matters have resulted in much discussion in the literature on uranium purification.¹⁶⁴⁻¹⁶⁶

Figures 4.7 and 5.1 allow the situation to be assessed for boron extraction. As can be seen there was very little difference regardless of pH in the equilibrium % extraction of boron (within 5-10%) obtained for clear solutions in the pulse column and shake-flasks in comparison with that of solutions containing bentonite or quartz. It was noted however that the pulse column resulted in curves consistently above those for the shake flasks - that is, the % extraction obtained was greater under the steady state pulse conditions than under shake flask equilibrium conditions. Although substantial random errors were to be expected in the (estimated) range 2-5% on account of the nature of the experimental conditions (particularly as a result of the critical and capricious variation of pH), and, indeed, such errors are evident in the crossing of the pulse column

curves (Figs. 4.7 and 5.1), there nevertheless appears to be a significant systematic difference involved, which is difficult to identify with certainty. Several factors may be contributing. Firstly, the shake-flask experiments were necessarily carried out separately and at a different time. Secondly, the contents in the column, of course, come to a different type of equilibrium compared with that in the shake-flasks. Thus, the column, efficiently operated, can be considered to facilitate some twenty 'stages' of extraction each to a first approximation, having its own chemical environment. Counter-current extraction in this way may well achieve better recovery than a single batch equilibration, and, if each stage reached equilibrium, it should be much better. In this respect the kinetics of extraction caused a potential problem because the retention time of organic bubbles in between two column disks was usually less than 1 minute, and this could not be substantially increased without disrupting the distribution of the bubbles in the column. Overall the column acted rather like a single stage batch equilibration. A third factor is the likelihood of boron being adsorbed from aqueous solution onto suspended solids which are then transferred into the organic phase. Although this effect must be small in the present case, because the quantity of solids transferred is small (see later), it is a well documented phenomenon¹⁶⁷⁻¹⁷¹.

Under the pulse conditions used, the phase separation appeared acceptably sharp and there was no evidence of emulsification. However, some solids and water were transferred and the organic layers were slightly turbid in the decreasing order CTMP > CTMP/EHD > EHD. The photographs in Fig. 5.10 (a)-(e) illustrate this point and Fig. 5.2 gives quantitative turbidimetric data in confirmation. Although it will be seen

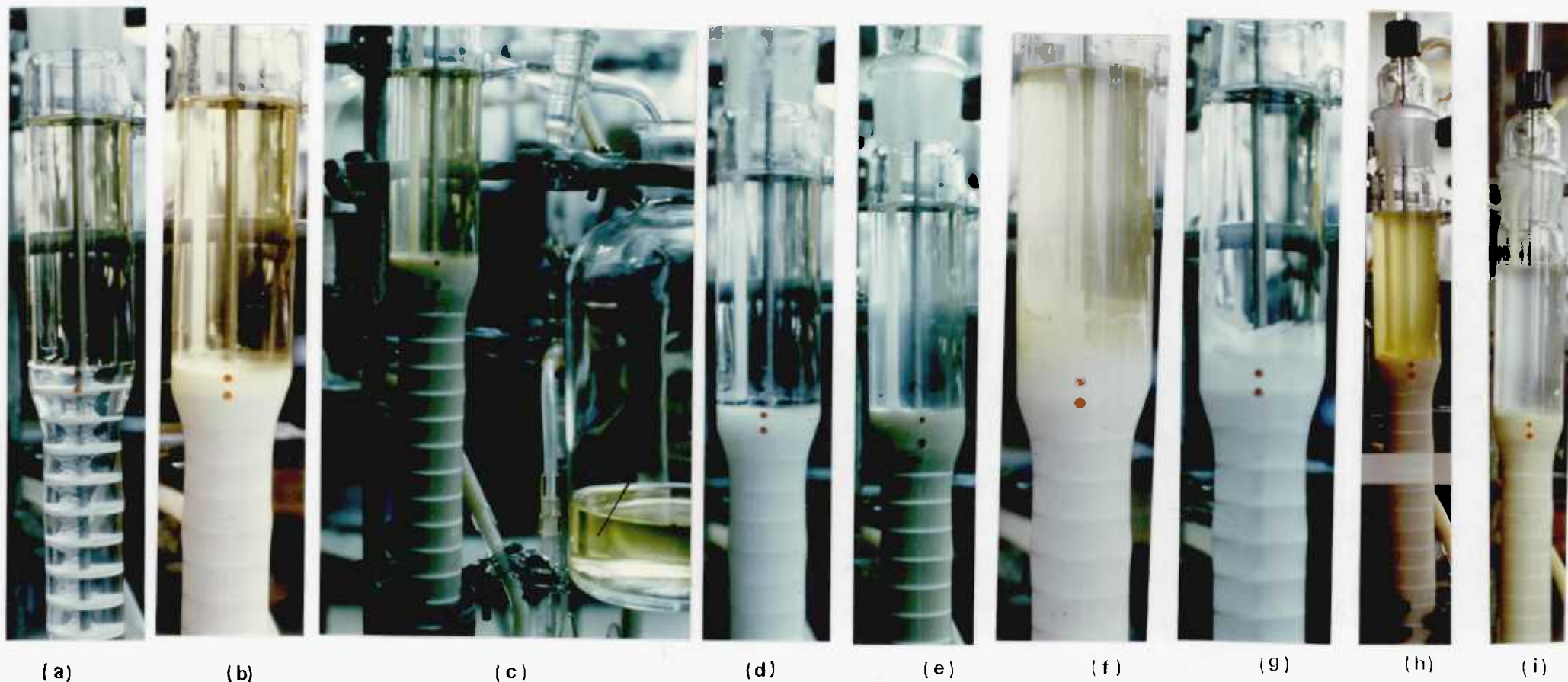


Fig. 5.10 Photographs illustrating phase separation in the sieve-plate-pulse column during pumping: (a) clear solutions/CTMP, (b) quartz slurry/CTMP, (c) bentonite slurry/CTMP (organic overflow stream arrowed), (d) quartz slurry/EHD, (e) bentonite slurry/EHD, (f) calcite slurry/CTMP, (g) calcite slurry/EHD, (h) Kirka slurry/CTMP and (i) Kirka slurry/EHD.

that such data are not necessarily a good means of estimating the precise quantity of solids present in the organic phase, they nevertheless give a useful comparison of phase clarity and show that in the cases considered the level of clarity is acceptable regardless of pH. The transmittance evidently decreased with ^{/increase in} pH but did not drop below about 75% .

Data for calcite could not be included in Figures 4.7, 5.1 and 5.2 because the mineral undergoes 'oil' flotation into the organic phase. Although with very careful operation a clear organic overflow could sometimes be obtained (despite the solids near the interface) - Fig. 5.10(f) - a very turbid overflow was normally obtained - Fig. 5.10(g) - particularly when CTMP was present. The Figures do not consider solid borate phases either because they would tend to dissolve in the organic phase, and confuse the results. However, Fig. 5.10(h) and (i) illustrates the (increased) turbidity obtained when the Kirka slurry (containing various minerals including borates and calcite) was extracted under the same conditions. These matters are considered in more detail further on.

In order to simulate with one column the multi-column counter-current operation which would probably be favoured industrially for pollution control, the column was used for successive extractions with the aqueous phase (only) in closed-circuit. Although such a course did not permit construction of a full McCabe Thiele diagram ¹⁵⁹ it did nevertheless indicate the number of 'pure solvent' stages required to reduce the boron level sufficiently in a raffinate - if it be assumed that the column acts similarly to a single batch equilibrium stage - and the number will not be greatly different in full counter-current operation. Figures 5.3 - 5.5 show results obtained with bentonite and the Kirka slurry, these being considered

as the most representative of the slurry phases. The figures contain extraction data both as a % of total boron (boxes) and cumulative % (dashed lines). It is evident that EHD, CTMP and CTMP/EHD require 5, 4 and 3 stages respectively to reduce the boron content to less than 5 ppm, and this gives a further indication of the synergistic effect which operates in this solvent system. The results can be related to equilibrium diagrams of the type given in Fig. 4.12. - as shown for one example in Fig. 5.11. From Figs. 5.4(b) and 5.5 the corresponding number of stages are 7, 5 and 4 the greater magnitudes resulting from the increased aqueous phase concentration and (probably) dissolution of solid boron minerals. Considering Fig. 5.3(a): the 1st stage extraction resulted in some 62% of the total boron transferred to the organic phase; the 2nd stage some 25% of the total; the 3rd some 8%, etc., leading to a total extraction of about 99% after 5 stages. By curcumin assay the final raffinate was found to contain 2-3 ppm B. Similarly for CTMP and CTMP/EHD the figures were 1.3 ppm (4 stages) and 0.9 ppm (3 stages) respectively.

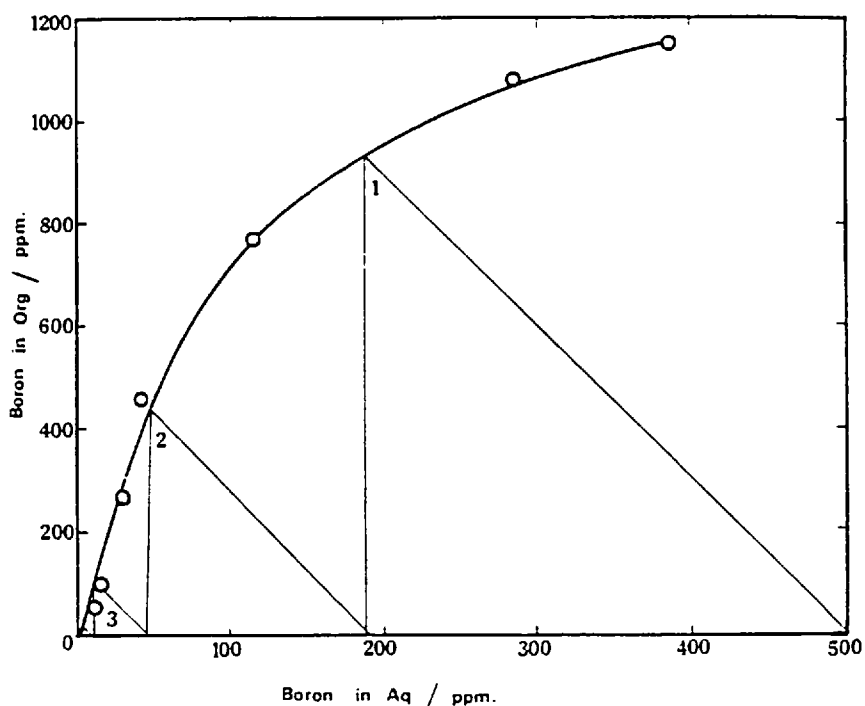


Fig. 5.11 Estimates of the number of stages needed to reduce boron in solution to below 5 from 500 ppm with CTMP/EHD (0.5 M).

On successive extraction of the bentonite slurry there was little change in the turbidity of the organic phases but with the extraction of Kirka slurry the turbidity varied markedly - as shown in Fig. 5.6. There is relatively great turbidity in the 1st stage and successively less at each succeeding stage in all three cases, although in the decreasing order CTMP > CTMP/EHD > EHD. This was attributed to the progressive removal of carbonate minerals from the aqueous phase: washing of the separated organic phases with dilute hydrochloric acid removed some of the turbidity. It should be noted that the turbidity figures represent the effect of a combination of minerals and water, and not just that of calcite.

Returning again to the matter of the clarity of the organic phases, attempts were made to assess quantitatively the amounts of the different solids transferred across the interface. Figures 5.7 and 5.8 show 'standard' curves of transmittance against concentration of solid suspension for EHD, CTMP and the mixed solvents for quartz, bentonite and water. Phase clarity is best for EHD and worst for CTMP; and is reduced by solids in the order quartz > bentonite > water. This qualitative order is not unexpected in view of the simple optical properties of the substances involved. Mixing quartz and water together might be expected to produce an additive turbidity effect - thus, 200 g m^{-3} for water and quartz separately produces (Fig. 5.8) derived absorbances of 0.12 and 0.26 respectively. The observed combined curve gives a corresponding value of 0.46. Some extra turbidity is developed on mixing the immiscible phases and its origin is obscure. In the case of bentonite/water mixtures concentrations of the former in excess of 100 gm^{-3} caused massive flocculation of the bentonite when water was present. Presumably this

resulted from a strong interaction between the dry bentonite and water, leading to precipitation and a relatively clear organic phase.

The results above indicated that the preparation of standards to estimate quantities of solids transferred during solvent extraction is not simple. However, combining the data in Fig. 5.2 (observed turbidities on extraction) with the curves in Figs. 5.7 and 5.8 rough estimates may be made. Thus, in the case of extraction from bentonite slurry at pH 9 the % solids in the organic phase are 0.4, 0.3, and 0.1 for CTMP, CTMP/EHD and EHD respectively, assuming that the solids content in the aqueous phase is $50,000 \text{ gm}^{-3}$. Values are of course lower at lower pH. For quartz slurries the corresponding figures are: 0.3, 0.2 and 0.05.

These estimates were considered sufficiently precise for preliminary discussion of a flowsheet and no attempt was made to obtain more precise data by direct weighing techniques.

Solvent losses to the aqueous phase result from dissolution, adsorption and entrainment of extractant and diluent. As inferred previously (section 5.3) only CTMP can be reliably determined at the low levels encountered in association with water solutions and suspensions. For this reason EHD losses have not been considered, although a published result¹²⁴ gives a (high) water solubility of 4.2%.

Figure 5.9 gives the results of CTMP solubility measurements at different pH values. The quantities dissolved at equilibrium increased sharply with pH but remained at only 16 ppm at pH 9. The spectrophotometric method appeared to work efficiently and the measurements should be reliable to better than $\pm 5\%$. Adsorption and entrainment were also measured by this method although the increased number of preliminary

Addendum

Lucas and Ritcey¹⁷⁸ claim that amine losses in solvent-in-pulp extraction of uranium from Elliot Lake leach slurry can be much reduced by suitable addition of non-ionic proteins or carbohydrates together with conventional flotation depressants such as sodium fluorosilicate, sodium silicate or sodium carbonate. Thus, losses of the solvent could be kept to 0.08 pounds per ton of dry solids (lb/tds) by (a) conventional flotation of sulphidic crud -forming slimes and (b) pulp conditioning successively with sodium fluorosilicate and fish glue, both at 0.5 lb/tds. This is to be compared with untreated losses of up to 5 lb/tds and a 'break-even' value of 0.1 lb/tds.

No account was taken in the present work of such a wide range of reagents capable of increasing the hydrophilic character of solids in boron-containing pulps. However, quebracho at up to 2 kg/tds, sodium silicate at 1 kg/tds, EDTA at 1 kg/tds and sodium carbonate 11 kg/tds did not have a significant effect on the oil flotation of carbonates.

manipulations may have reduced precision. Results for adsorption onto the various mineral phases considered (Table 5.2) show that the affinity for CTMP increases in the order quartz < clays < carbonates but is largely independent of pH in the range 5/7 - 11/12. For quartz and clays adsorption and solubility losses are roughly of the same order. Thus, at pH 9 the solubility is 16 ppm while the adsorption is about 9 (quartz) and 13 (bentonite). It is assumed that the hydrophilic minerals interact preferentially with water but rough calculations matching their available surface areas (Table 5.1) with the observed adsorptions of CTMP indicate that while the quartz surfaces may be associated with a double layer of the solvent, those of bentonite have considerably less than a monolayer. The extent of adsorption on carbonates is much greater and may involve full reaction of the species to form calcium complexes, limited only by the rate of interaction. Clearly the presence of significant quantities of the carbonates would cause problems in a CTMP solvent extraction system.

Table 5.2 gives the combined effect of carbonate minerals and others in the Kirka slurry, the overall adsorption being 29.5 ppm (about twice the solubility loss at pH 9.2).

(see opposite)

Attempts to modify the carbonate surfaces/by interaction with flotation depressants did not meet with success (the reagents quebracho, sodium silicate, EDTA and sodium carbonate were used), and prior separation of carbonates would probably be necessary if significant amounts (greater than about 1.5% of the total slurry) are present. It should be feasible to carry out such a separation either by conventional or oil flotation^{172,173}. Alternatively, oil flotation could be considered as an integral operation with the solvent extraction process.

With regard to entrainment, reliable figures are difficult to obtain with small scale apparatus, but approximate ones were obtained by means of the method given in section 5.3. Thus the two slurries tested (bentonite and Kirka) gave similar results at just over 100 gm^{-3} , while corresponding clear solutions gave 46 g m^{-3} . These values are predominant when compared with those of solubility and adsorption, and, although such a result must be expected, it is considered that the present method of determining entrainment probably gave high results.

Combining the figures obtained for solubility, adsorption and entrainment as found, the total losses are estimated to be 136 and 152 g CTMP per m^3 of slurry (0.3 and 0.33 lb ton^{-1}) for bentonite and Kirka slurries respectively. These losses are probably too great to be tolerated on grounds of cost and pollution,¹⁷⁴ and some form of recovery, perhaps by solvent flotation¹⁷⁵, would need to be incorporated.

It is estimated that 40 tonne per hour of Kirka slurry reaches the tailings pond⁷³. This mixture is saturated with borax (0.46 M) and will contain low concentrations of calcium and magnesium in accordance with the solubility products of the corresponding borates and carbonates. The solids content is roughly 4.5%, made up mainly of clays (52%), carbonates (32%), borates (6%) and others (9%). Owing to the large montmorillonite/hectorite/illite content of the solids the slurry cannot be effectively thickened despite addition of large concentrations of flocculant. If boron pollution is to be avoided the effluent must either be effectively impounded (which appears to be impracticable in the long term) or subjected to solvent in-pulp extraction as described in a preliminary manner herein. There

can be little prospect of making such a process economically viable because the recovered borax would be of relatively minor value and it could only go ahead on environmental grounds.

Considering the best conditions for solvent extraction deduced from the present work the solvent used would be a 1:1 mixture of EHD and CTMP at 0.5 M (total) in kerosene and the extraction would be carried out at pH 9.2 in 3-4 pulse column stages. These conditions should permit advantage to be taken of the synergistic effect operating between the two solvents at the natural pH of the slurries to give a raffinate of 5-10 ppm B. It is assumed that some dilution would occur naturally in the drainage system so that the effluent reaching nearby irrigation channels would be non-toxic.

The effective column capacity and flow rate used on the laboratory scale were 300 cm^3 and 5 cm^3 per minute respectively. In order to accommodate a flow rate of 40 tonne per hour with plant of the same height to diameter ratio (16), two columns 20 m in height and 1.25 m in diameter are required (on the basis of the simplest of calculations). The loaded solvent may be stripped on the laboratory scale by use of 2 M hydrochloric acid in 1:1 aqueous to organic ratio in three stages. As any suspended carbonates would dissolve in this medium, it should be feasible to employ conventional mixer-settlers. On the basis of published¹⁴⁸ work three units of equipment of volume 2 and 5 m^3 would be required for mixers and settlers respectively.

A basic flowsheet is given in Fig. 5.12 which should produce roughly 4.5 tonne boric acid per day, by techniques similar to those adopted at Searles Lake⁶⁷. It is not feasible on the basis of data available

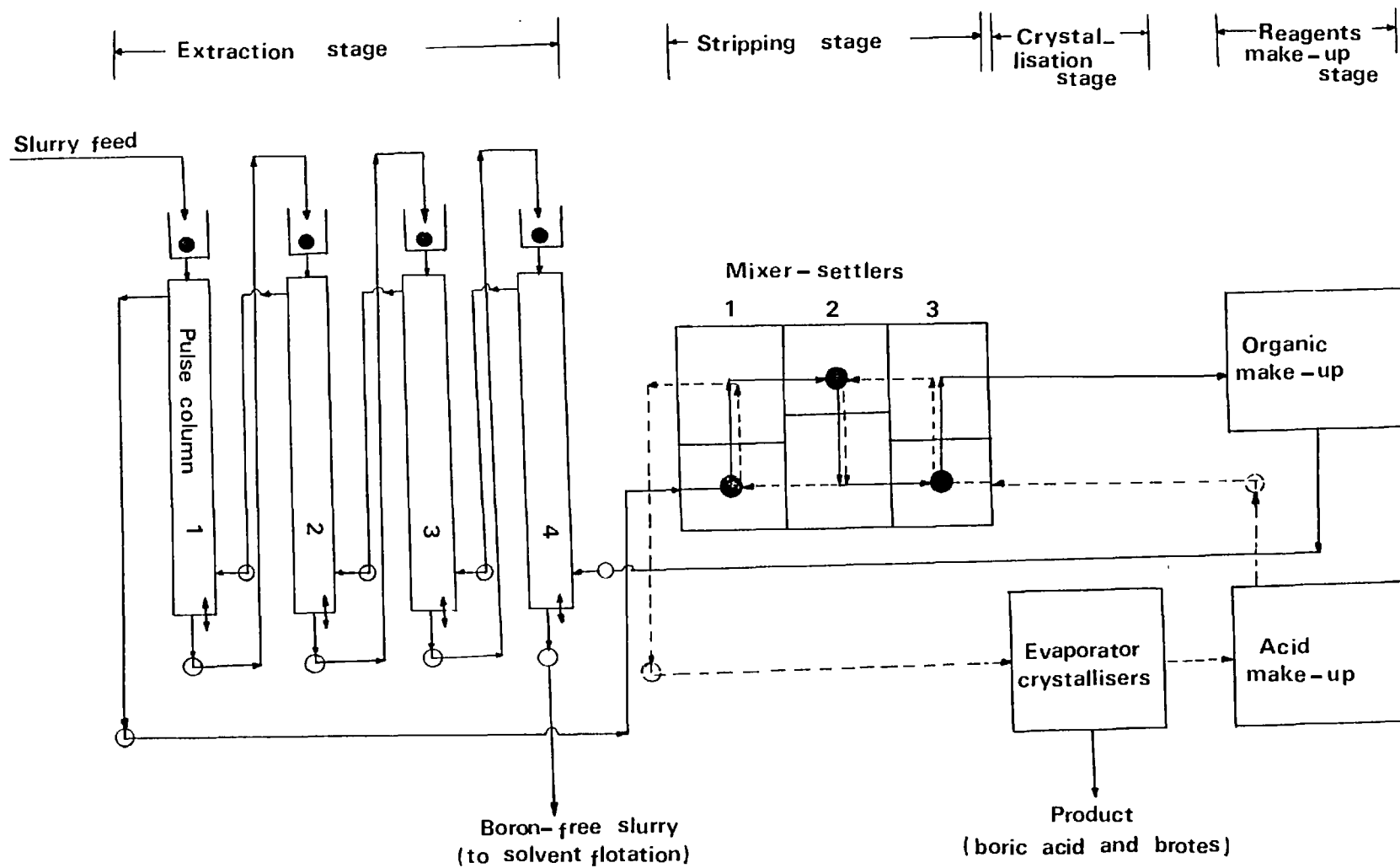


Fig. 5.12 A proposed flowsheet for solvent-in-pulp extraction of boron from Kirka slurry.

from the present work to give a detailed flowsheet but some general comments can be made:

- (1) the boron-free slurry would need to be treated to recover entrained solvent.
- (2) the boric acid would be recovered by evaporation and recrystallisation in evaporator-crystallisers⁶⁷ at the same time regenerating the acid for recycle to stripping.
- (3) continual acid make-up would be required to replace that lost through interaction with carbonates (in addition to borates). This appears to be preferable to installing extra plant to filter the suspended carbonates. Organic make-up would also be necessary.
- (4) over a period of time the sodium, calcium and magnesium content of the strip liquor would build up and result in the precipitation of borates of these metals, in addition to boric acid. The mixed product would be acceptable at the refineries.
- (5) on the basis of the laboratory pulse column experiments crud formation at interfaces would not be expected to occur to a significant extent.

It is not the purpose in this thesis to produce a detailed flowsheet with itemized equipment and costs. Further test work employing larger scale counter-current plant would be required first, together with a critical study of the question of solvent losses and regeneration. Methods should be sought in particular to render hydrophilic the surfaces of suspended particulate matter in boron-containing pulps by methods analogous to those given by Lucas and Ritcey¹⁷⁸. It can be concluded from the present work that such test work should be undertaken as the next step.

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