Complexation of platinum, palladium and rhodium with inorganic ligands in the environment

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ABSTRACT: Platinum (Pt), palladium (Pd) and rhodium (Rh) are emitted by vehicle exhaust catalysts (VECs) and their concentrations have increased significantly in various environmental compartments, including airborne particulate matter, soil, roadside dust, vegetation, rivers and oceanic environments, over the last two decades as the use of VECs has increased. However, data on the chemical speciation of the platinum-group elements (PGEs) and their bioavailabilities are limited. In this paper, the thermodynamic computer model, HSC, has been used to predict the interactions of Pt, Pd and Rh with different inorganic ligands and to estimate the thermodynamic stability of these species in the environment. Eh–pH diagrams for the PGEs in aqueous systems under ambient conditions (25°C and 1 bar) in the presence of Cl, N and S species have been prepared. The results indicate that Pt, Pd and Rh can form complexes with all of the inorganic ions studied, suggesting that they are capable of mobilizing the PGEs as aqueous complexes that can be transported easily in environmental and biological systems and that are able to enter the food chain. Hydroxide species can contribute to the transport of PGEs in oxidizing environments such as road-runoff waters, freshwater, seawater and soil solutions, whereas bisulphide complexes could transport Pt and Pd in reducing environments. Ammonia species appear to be significant under near-neutral to basic oxidizing conditions. Chloride species are likely to be important under oxidizing, acidic and saline environments such as seawater and road-runoff waters in snowmelt conditions. Mixed ammonia–chloride species may also contribute to the transport of Pt and Pd in highly saline solutions.

KEYWORDS: *platinum group elements, thermodynamics, inorganic ligands, environmental impact*

INTRODUCTION

The platinum-group elements (PGEs) have unique chemical and physical properties that have led to a wide range of uses over the past 30 years. The main use of the PGEs presently is in vehicle exhaust catalysts (VECs), but there are many other diverse uses including jewellery, medicine, electronic and chemical industries, glass production and gasoline refining. Furthermore, the introduction of fuel cell technology for energy generation is likely to further increase the demand for these rare elements (Vermaak 1995; Hilliard 2003; Kendall 2004).

Autocatalysts using Pt, Pd and Rh to convert noxious exhaust emissions into less harmful gases are now fitted routinely to vehicles throughout the developed world. Conventional three-way catalytic converters typically contain 0.08% Pt, 0.04% Pd, and 0.005–0.007% Rh, corresponding to 1–5 g of PGEs per vehicle (Vermaak 1995). The USA and Japan were the first countries to enact standards that required the fitting of catalysts to passenger cars, with Europe, Australia and parts of Asia following in the 1980s. Since the 1990s, some developing countries, including Brazil, Mexico and India, have required the use of VECs. Today, more than half of the world's 500 million

cars have such catalysts fitted, and more than 90% of new cars sold worldwide have a catalytic converter as standard equipment. Legislation governing emissions from vehicles continues to tighten, in both the mature car markets of Europe, North America and Japan, as well as in rapidly developing markets such as those of China and India, so that considerable future growth in the use of PGEs in autocatalysts is predicted (Hilliard 2003; Kendall 2004).

Although VECs were introduced to combat air pollution, there is now growing concern that their use may, in itself, represent a significant source of pollution. Indeed, there is accumulating evidence that PGEs are released from autocatalysts and that concentrations of these metals have increased significantly over the last two decades in various environmental compartments, including in the air as airborne particulate matter, in roadside dusts, soils, river and oceanic sediments and in vegetation. According to Barefoot (1999), the concentration of Pt in soils near German roads is now *c.* 70 times higher than background values. Increases in PGE concentrations have also been measured in UK towns over the period 1982–1998 (Farago *et al.* 2000; Hutchinson *et al.* 2000). Most industrial processes, including PGE refining and the manufacture of

autocatalysts, chemicals and jewellery, have limited and local areas of environmental impact, partly because the intrinsic value of PGEs means that great care is taken to avoid significant losses at all stages of mining, refining and manufacture. In contrast, the emissions from autocatalysts represent a highly dispersed source of environmental contamination of Pt, Pd and Rh.

PGEs are emitted from VECs mainly as fine particulate material from the abrasion and deterioration of the catalyst surface, and these particles are deposited as dust on roads and adjacent vegetation and surfaces (Kummerer *et al.* 1999). The annual worldwide emission of Pt, arising solely from automobile catalytic converters, has been estimated at 0.5–1.4 tons per year (Barbante *et al.* 2001). It has been suggested that *c.* 99% of the Pt released from VECs is in the metallic state, with only *c.* 1% present as oxidized Pt, presumably as PtO₂ (Schlogl *et al.* 1987; Artelt *et al.* 2000). Early experiments also revealed that some volatile Pt(IV) oxide is formed when Pt metal is heated to 500°C in contact with either air or oxygen (Balgord 1973). The assertion that PGEs are released mostly in metallic form has been challenged recently, based on solubility experiments of PGEs in roadside dusts (Jarvis *et al.* 2001), which concluded that PGEs may not be in metallic form in exhaust fumes and/or that they can be transformed rapidly in a soluble form through complexation by chloride or possibly humic matter following deposition in the environment. Nachtigall *et al.* (1996) observed that the low solubility of emitted Pt in deionized water increased significantly on addition of certain anions including Cl[−] and CN[−]. Also Fuchs & Rose (1974) studied the geochemical behaviour of naturally occurring Pt in soil: Pt showed considerable mobility only in extremely acidic chloride-rich soils, suggesting the presence of divalent Pt as PtCl₄^{2−}.

Platinum-group metals in the elemental state have low toxicities and are unreactive in most environments, but some of their chemical compounds are allergenic or even cytotoxic (WHO 1991, 2002). The speciation of PGEs in the environment is key to understanding their biogeochemical mobilities and transformations, and their pathways and toxicity to receptors such as humans. This is poorly understood and data concerning the distribution and behaviour of PGEs in the environment, and their chemical speciation and bioavailability, are limited.

The pathways and fate of metals depend upon their chemical properties and those of the surrounding air, water, sediment or soil. This paper describes thermodynamic studies of the behaviour of the PGEs in the presence of inorganic ligands common in the environment (such as hydroxide, sulphide, ammonium, chloride) to better understand the hazards and risks posed by the widespread use of the PGEs especially in VECs.

METHODOLOGY

A thermodynamic model (HSC Chemistry[®] for Windows, Outokumpu, Version 4.0) was used to calculate the interactions of Pt, Pd and Rh with different inorganic ligands, the formation of stable PGE species, and the thermodynamic stability of these species in the environment. HSC Chemistry[®] for Windows software is designed for various kinds of chemical reaction and equilibrium calculations; the name of the program reflects the use of a thermochemical database which contains values of enthalpy (H), entropy (S) and heat capacity (C). Thermodynamic data for complexes of PGEs with most common inorganic ligands are available in the software's database. These data were examined and found to be the same as those reported in the National Bureau of Standards (NBS) tables (Wagman *et al.* 1982) and the Russian tables, *Thermal Constants of Substances*

(Medvedev 1965). Additional data pertinent to PGE complexes from these tables were also added to the software database. Both the NBS and the Russian tables contain critically evaluated and reliable values of chemical thermodynamic properties. Where appropriate, further data (Cozzi & Pantani 1958; Forrester & Ayres 1959; Nabivanets & Kalabina 1970; Mountain & Wood 1988; Byrne & Kump 1993; Wood *et al.* 1994; van Middlesworth & Wood 1999; Byrne & Yao 2000; Wood 2002) were also added to the database. These data are tabulated in the Appendix and are discussed in the Results section.

The HSC program was used to construct Eh–pH diagrams for the PGEs in aqueous solution at ambient conditions (25°C and 1 bar) in the presence of inorganic ligands commonly found in the environment. The most common oxidation state of Rh is +3, whereas Pt and Pd can occur in either the +2 or the +4 valence state in aqueous solution. The divalent state largely predominates over the tetravalent state at 25°C, except under extremely oxidizing conditions (Hartley 1992). Theoretical studies (Plimer & Williams 1987; Mountain & Wood 1988; Wood 2002) have identified hydroxide, chloride, sulphide and ammonia as of possible importance in the complexation of Pt²⁺, Pd²⁺ and Rh³⁺. In contrast, the weakly polarizable ligands CO₃^{2−}, HCO₃[−], SO₄^{2−} and PO₄^{3−} complex only very slightly, if at all, with the strongly polarizable Pt²⁺, Pd²⁺ and Rh³⁺ ions (Mountain & Wood 1988; Hartley 1992) and they are therefore not considered further in this study. Platinum, Pd and Rh form strong complexes with Br[−], I[−], CN[−] and SCN[−] (Plimer & Williams 1987). The concentration of these anions in the most common environmental compartments is likely to be relatively small, however, and so their PGE complexes are also not considered in this paper.

The total dissolved PGE concentration was fixed at 10^{−9} M. The inorganic ligand concentrations were chosen to reflect ambient environmental concentrations. The values are: [S]=10^{−6} to 10^{−3} M, [NH₃]=10^{−6} to 5 × 10^{−4} M and [Cl]=10^{−5} to 10^{−3} M for road runoff, freshwater and soil solutions, respectively, and [Cl]=0.5 M for highly saline solution such as seawater and road runoff in snowmelt conditions (Brookins 1988; Stumm & Morgan 1996; Drever 1997; Howard & Hayes 1997; Agency for Toxic Substances & Disease Registry 2004a, b; Mangani *et al.* 2005; US Environmental Agency 2006).

RESULTS

PGEs in water

Figures 1, 2 and 3 show the Eh–pH diagrams for Pt, Pd and Rh in water, respectively, the thermodynamic stability of which is shown by dotted lines. Since all the conditions above the upper, and below the lower, water stability line are metastable, the Eh–pH diagrams are discussed only in relation to species within the field of water stability.

Despite the known tendency of Pt, Pd and Rh to form hydroxide complexes, reliable thermodynamic data for these species are difficult to obtain due to the propensity of the PGEs to form insoluble hydroxides or oxides. Because of the lack of reliable thermodynamic constants for the whole range of possible hydroxide complexes, the determination of the contribution of PGE-hydroxides to PGE solubility will involve uncertainties.

Figure 1 shows that native Pt(s) occupies most of the Eh–pH range. Stability constants for Pt hydroxide complexes were estimated from linear free energy relationships (Wood *et al.* 1989): log β₁=14.2, log β₂=28.3, log β₃=30.8 and log β₄=32.0. These values agree well with the stability constants obtained by Wood (1991) through solubility experiments. PtO₂(s)

Fig. 1. Eh–pH diagram for Pt in aqueous solution with $[\Sigma\text{Pt}]=10^{-9}$ M. Light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

Fig. 2. Eh–pH diagram for Pd in aqueous solution with $[\Sigma\text{Pd}]=10^{-9}$ M. Light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

predominates near the upper stability limit of water. On the other hand, through solubility measurements, Azaroual *et al.* (2001) derived $\log \beta_1=24.91$. Byrne (2003) commented on this discrepancy and found the estimate of Azaroual *et al.* (2001) greatly in error. Therefore the values obtained by Wood *et al.* (1989) were employed in the construction of the Eh–pH diagram depicted in Figure 1. The $\text{Pt}(\text{OH})^+$ species occurs under very acidic and highly oxidizing conditions while the predominance field for $\text{Pt}(\text{OH})_4^{2-}$ is restricted to highly basic, slightly oxidizing conditions. $\text{Pt}(\text{OH})_2(\text{aq})$ is the predominant dissolved species in a wide range of pH ($1 < \text{pH} < 12$). These observations are in agreement with the findings of Sassani & Shock (1998) and Byrne (2003) who concluded that hydroxide complexes could contribute significantly to the solubility of Pt in aqueous solutions.

The Eh–pH diagram for Pd is shown in Figure 2. Nabivanets & Kalabina (1970) reported experimental values for the Pd–hydroxide species, determined at 25°C in 0.1M NaClO_4 . These values are in agreement with those reported by van Middlesworth & Wood (1999) and by Izatt *et al.* (1967) and have been used in the construction of the Eh–pH diagrams: $\log \beta_1=11.7$, $\log \beta_2=23.6$, $\log \beta_3=25.4$ and $\log \beta_4=26.4$. A large predominance field is occupied by native Pd. This oxidizes to Pd^{2+} under oxidizing, acidic conditions or to $\text{Pd}(\text{OH})_3^-$ and

Fig. 3. Eh–pH diagram for Rh in aqueous solution with $[\Sigma\text{Rh}]=10^{-9}$ M. Heavy solid lines separate stability fields of solid phases, light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

$\text{Pd}(\text{OH})_4^{2-}$ under extremely basic conditions. $\text{Pd}(\text{OH})_2(\text{aq})$ is the predominant dissolved species in a wide range of pH ($2 < \text{pH} < 12$).

Thermodynamic data for Rh hydroxide species were taken from Forrester & Ayres (1959), Plumb & Harris (1964) and the most recent update of the Common Thermodynamic Database (2006). No thermodynamic data are available for Rh–hydroxide aqueous complexes. The Eh–pH diagram for Rh (Fig. 3) shows that native $\text{Rh}(\text{s})$ occupies a wide predominance field and oxidizes to Rh^{3+} in extremely acidic environments or to $\text{Rh}(\text{OH})_3(\text{s})$.

It is evident from the Eh–pH diagrams for the PGEs in water that the hydroxide complexes may be important in transporting PGEs in oxidizing surface environments.

PGE–S system

Mountain & Wood (1988) were the first authors to propose that bisulphide complexes might be important in the transport of Pt and Pd. According to Wood *et al.* (1994), the predominant species at low temperatures in concentrated bisulphide solutions are most likely to be $\text{Pt}(\text{HS})_2(\text{aq})$ and $\text{Pd}(\text{HS})_2(\text{aq})$. Such bisulphide complexes could transport Pt and Pd and could lead to the formation of Pt and Pd solid phases such as sulphides.

Figures 4–6 show the Eh–pH diagrams for the PGE–S system. Wood *et al.* (1994) and Gammons & Bloom (1993) studied the solubility of Pt and Pd sulphides in bisulphide solutions and both authors measured similar magnitudes of solubilities. The thermodynamic data for Pt and Pd bisulphide complexes used in the construction of the Eh–pH diagrams are from Wood *et al.* (1994) and the data for the sulphide compounds are from the NBS tables (Wagman *et al.* 1982). No thermodynamic data are available for Rh–bisulphide complexes. Figures 4a, 5a and 6 indicate the ability of the PGEs to form sulphide with the predominance field of the sulphide compounds decreasing slightly with decreasing $[\text{S}]$. The strongly polarizable nature of Pt^{2+} , Pd^{2+} and Rh^{3+} means that their complexes with the weakly polarizable anion SO_4^{2-} have low stability. Indeed, the only available stability constant for such complexes, that of $\text{Pd}(\text{SO}_4)_2^{2-}$ at 25°C, is small (Hogfeldt 1982). In contrast, PGEs are predicted to form strong complexes with the strongly polarizable bisulphide anion as shown in the Eh–pH diagrams illustrating the predominance field of the aqueous sulphur species (Figs. 4b and 5b).

Fig. 4. (a) Eh–pH diagram for the Pt–S system with $[\Sigma\text{Pt}]=10^{-9}$ M and $[\Sigma\text{S}]=10^{-3}$ M. (b) The predominance field of the aqueous sulphur species. Heavy solid lines separate stability fields of solid phases, light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

PGE–N system

The Eh–pH diagrams for the Pt– and Pd–nitrogen systems are shown in Figures 7 and 8, respectively. No data for Rh–N species are available in the thermodynamic databases, so that the Rh diagram could not be constructed, although ammonia–Rh complexes are known to exist. For example, Skibsted & Ford (1980) studied the dissociation of aqua–amminerhodium(III) complexes, but the stability constants of these complexes have not been determined.

Thermodynamic data on Pt– and Pd–ammonia complexes were added to the database. The cumulative stability constants for the Pt and Pd tetrammonia complexes at 25°C are: $\log \beta_4=35.3$ for Pt^{2+} (Grinberg & Gel’fman 1961) and $\log \beta_4=32.6$ for Pd^{2+} (Rasmussen & Jorgensen 1968). The values of these stability constants are relatively large and therefore ammonia complexes might be expected to be significant in the transport of these metals. Thermodynamic data for mixed ammonia–hydroxide complexes of Pt have been taken for the NBS tables (Wagman *et al.* 1982). Figures 7 and 8 illustrate the stability of Pt and Pd tetrammine complexes. The predominance fields of the ammonia complexes vary significantly with the nitrogen concentration: they disappear at $[\text{N}] < 6 \times 10^{-5}$ M for Pt and

Fig. 5. (a) Eh–pH diagram for the Pd–S system with $[\Sigma\text{Pd}]=10^{-9}$ M and $[\Sigma\text{S}]=10^{-3}$ M. (b) The predominance field of the aqueous sulphur species. Heavy solid lines separate stability fields of solid phases, light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

$[\text{N}] < 2 \times 10^{-5}$ M for Pd. The Eh–pH diagrams also show that the predominance field of ammonia complexes is wider and hence the potential for transport as ammonia complexes is greater for Pd than for Pt. The mixed ammonia–hydroxide complex $\text{Pt}(\text{NH}_3)_2(\text{OH})_2(\text{aq})$ occupies a very small predominance field at basic pH.

Figures 7 and 8 were calculated assuming that the kinetics of the oxidation of ammonia to nitrogen are rapid, but ammonia may persist in a metastable state outside its thermodynamic predominance field (Wood 2002) which would increase its importance as a potential ligand for PGEs.

PGE–Cl system

Wood *et al.* (1992) and Sassani & Shock (1998) critically reviewed many investigations on the complexing of Pt and Pd by chloride. The various studies reported significantly different thermodynamic constants and the aforementioned authors disagree on which stability constants to recommend for both Pt and Pd–chloride complexes. Although there is poor quantitative agreement, qualitatively both data sets lead to the same conclusion: that significant solubilities of Pt and Pd as chloride complexes will occur only in highly oxidizing, acidic conditions.

Fig. 6. Eh–pH diagram for the Rh–S system with $[\Sigma\text{Rh}]=10^{-9}$ M and $[\Sigma\text{S}]=10^{-3}$ M. Heavy solid lines separate stability fields of solid phases, light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

Fig. 7. Eh–pH diagram for the Pt–N system with $[\Sigma\text{Pt}]=10^{-9}$ M and $[\Sigma\text{N}]=5 \times 10^{-4}$ M. Light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

In the construction of the Eh–pH diagrams in this paper, the thermodynamic data for the Pt– and Pd–chloride complexes were taken from the NBS tables (Wagman *et al.* 1982). These values are very similar to those suggested by Wood *et al.* (1992).

The Pt–Cl system is represented in Figure 9. The $\text{Pt}(\text{OH})_2(\text{aq})$ dissolved species predominates over chloride complexes over a wide range of pH, even at high chloride activities. Gammons (1996) studied the solubility of metallic Pt in HCl solutions and showed that the solubility of Pt decreased rapidly with increases in pH, suggesting that there is saturation with respect to a solid divalent or tetravalent Pt oxide or hydroxide. It is apparent from Figure 9 that the solubility of Pt under moderately oxidizing conditions, such as seawater, in which the chloride concentration is *c.* 0.5–0.8 M (Stumm & Morgan 1996), will be due mainly to Pt(II) tetrachloro complexes and, under highly oxidizing conditions, to Pt(IV) hexachloro complexes. These results are consistent with experimental results on Pt–chloride complexation (Gammons 1996). Gammons observed that the equilibrium between metallic Pt(0), Pt(II) and Pt(IV) in HCl solutions may be represented by a simple disproportionation reaction in which, at high chloride

Fig. 8. Eh–pH diagram for the Pd–N system with $[\Sigma\text{Pd}]=10^{-9}$ M and $[\Sigma\text{N}]=5 \times 10^{-4}$ M. Light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

Fig. 9. Eh–pH diagrams for the Pt–Cl system with $[\Sigma\text{Pt}]=10^{-9}$ M, $[\Sigma\text{Cl}]=0.5$ M (a) and $[\Sigma\text{Cl}]=10^{-3}$ M (b). Light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

Fig. 10. Distribution of Pt(II)-Cl species as a function of chloride concentration, with α representing the fraction of Pt(II) present as each species of Pt-chloride complex.

concentrations, the dominant Pt species are PtCl_4^{2-} and PtCl_6^{2-} .

The concentration of chloride ions is the dominant factor in the speciation of Pt(II) and, at high chloride concentrations (>0.5 M), the PtCl_4^{2-} species is predominant, whereas PtCl_3^- becomes important at relatively low chloride concentrations (10^{-2} M). Figure 10 represents the fraction (α) of Pt(II) present as each Pt-chloride complex as a function of the chloride ion concentration. Chloride complexes appear in the Eh-pH diagrams for the Pt-Cl system only when the chloride concentration is greater than 4×10^{-4} M.

The Eh-pH diagrams for the Pd-Cl system are illustrated in Figure 11. The $\text{Pd(OH)}_2(\text{aq})$ dissolved species predominates over the chloride complexes over a wide range of pH, even at high activities of chloride, and chloride complexes appear in the Eh-pH diagrams only when the chloride concentration is higher than 10^{-4} M. As in the Pt-Cl system, the concentration of the chloride ions determines which Pd species occurs (Fig. 12). Figure 12 shows that all the chloride species can contribute to Pd transport in the aqueous environment, with PdCl_4^{2-} predominating in saline solutions ($[\text{Cl}^-] > 1$ M).

Mixed hydroxy-chloride complexes of Pd(II) have been studied by many investigators (Tait *et al.* 1991; Byrne & Kump 1993; van Middlesworth & Wood 1999). Most of these studies indicate that $\text{PdCl}_3\text{OH}^{2-}$ is a minor species in solutions with chloride concentrations that approximate to those of seawater, except van Middlesworth & Wood (1999), who maintain that the $\text{PdCl}_3\text{OH}^{2-}$ species predominates over the entire pH range of natural seawater ($7.5 < \text{pH} < 8.5$). Byrne & Yao (2000) have suggested that this discrepancy is due to the unrecognized presence of a mixed hydroxychloride Pd(II) solid species, which controlled the solubility in the experiments of van Middlesworth & Wood, and concluded that PdCl_4^{2-} predominates over $\text{PdCl}_3\text{OH}^{2-}$ throughout the normal pH range of seawater.

Rhodium(III) forms octahedral complexes with anions such as halides and a variety of Rh aquo-chloro complexes exist in solution (Benguerel *et al.* 1996). The species range from the completely hydrated hexaquo-rhodium, $\text{Rh(H}_2\text{O)}_6^{3+}$, to hexachloro-rhodium, RhCl_6^{3-} , with intermediate mixed aquo-chloro complexes, $\text{RhCl}_{6-n}(\text{H}_2\text{O})_n^{n-3}$, also present. The extent to which each complex exists depends primarily on the chloride concentration. It has been found that, at high chloride concentrations ($[\text{Cl}^-] \approx 0.1$ M), the main Rh species are RhCl_6^{3-} and $\text{RhCl}_5(\text{H}_2\text{O})_2^{2-}$, although $\text{RhCl}_4(\text{H}_2\text{O})_2^-$ can also occur. As the chloride concentration decreases the hydration reactions occur more readily. Cozzi & Pantani (1958) conducted a

Fig. 11. Eh-pH diagrams for the Pd-Cl system with $[\Sigma\text{Pd}]=10^{-9}$ M, $[\Sigma\text{Cl}]=0.5$ M (a) and $[\Sigma\text{Cl}]=10^{-3}$ M (b). Light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

Fig. 12. Distribution of Pd(II)-Cl species as a function of chloride concentration, with representing the fraction of Pd(II) present as each species of Pd-chloride complex.

polarographic study of Rh chloride complexes and calculated the following stability constants: $\log K_1=2.45$, $\log K_2=2.09$, $\log K_3=1.38$, $\log K_4=1.16$, $\log K_5=1.6$, $\log K_6=-0.32$. The Eh-pH diagrams (Fig. 13) for the Rh-Cl system were constructed after adding these data to the main database. The hydroxide species, $\text{Rh(OH)}_3(\text{s})$, predominates over chloride complexes over a wide

Fig. 13. Eh-pH diagrams for the Rh-Cl system with $[\Sigma\text{Rh}]=10^{-9}\text{ M}$, $[\Sigma\text{Cl}]=0.5\text{ M}$ (a) and $[\Sigma\text{Cl}]=10^{-3}\text{ M}$ (b). Heavy solid lines separate stability fields of solid phases, light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

Fig. 14. Distribution of Rh(III)-Cl species as a function of chloride concentration, with α representing the fraction of Rh(III) present as each species of Rh-chloride complex.

range of pH, even at high chloride activities. Figure 14 illustrates the proportions of the Rh chlorocomplexes as a function of chloride activity. The main species are Rh^{3+} , RhCl_2^+ , RhCl_2^{2+}

Fig. 15. Eh-pH diagrams for Pt in aqueous solution with $[\Sigma\text{Pt}]=10^{-9}\text{ M}$, $[\Sigma\text{S}]=10^{-3}\text{ M}$, $[\Sigma\text{N}]=5 \times 10^{-4}\text{ M}$ and $[\Sigma\text{Cl}]=0.5\text{ M}$ (a) and $[\Sigma\text{Pt}]=10^{-9}\text{ M}$, $[\Sigma\text{S}]=10^{-3}\text{ M}$, $[\Sigma\text{N}]=5 \times 10^{-4}\text{ M}$ and $[\Sigma\text{Cl}]=10^{-3}\text{ M}$ (b). Heavy solid lines separate stability fields of solid phases, light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

and RhCl_5^{2-} , with RhCl_5^{2-} predominating in saline solutions ($[\text{Cl}^-] > 0.1\text{ M}$). Chloride complexes appear in the Eh-pH diagrams for the Rh-Cl system only when the chloride activity is greater than $4 \times 10^{-3}\text{ M}$.

PGE-Cl-N-S system

The behaviour of PGEs in solutions containing all of the inorganic ligands studied separately was also investigated. All the thermodynamic data for mixed-ligand species are taken from the NBS tables (Wagman *et al.* 1982). The behaviour of Pt in aqueous solution in the presence of sulphur, hydroxide, ammonia and chloride is shown in Figure 15. Sulphide compounds predominate near the lower stability limit of water. The composition of the simple Pt(II) chloride species depends on the concentration of chloride ions (Fig. 10). In highly saline solutions (Fig. 15a), PtCl_4^{2-} predominates in acidic oxidizing media, while PtCl_6^{2-} becomes important in more strongly oxidizing environments. With increasing pH, PtCl_6^{2-} transforms into $\text{Pt}(\text{NH}_3)\text{Cl}_5^-$ and then into $\text{PtO}_2(\text{s})$ in near-neutral and basic solutions. Mixed Pt(II)-ammine-chloride,

Fig. 16. Eh–pH diagrams for Pd in aqueous solution with $[\Sigma\text{Pd}]=10^{-9}$ M, $[\Sigma\text{S}]=10^{-3}$ M, $[\Sigma\text{N}]=5 \cdot 10^{-4}$ M and $[\Sigma\text{Cl}]=0.5$ M (a) and $[\Sigma\text{Pd}]=10^{-9}$ M, $[\Sigma\text{S}]=10^{-3}$ M, $[\Sigma\text{N}]=5 \times 10^{-4}$ M and $[\Sigma\text{Cl}]=10^{-3}$ M (b). Heavy solid lines separate stability fields of solid phases, light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

amine–hydroxide, simple hydroxide and simple ammonia complexes all contribute to the solubility of Pt in slightly less oxidizing solutions ($0.4 < \text{Eh} < 0.7$), in the pH range between 4 and 11, and the $\text{Pt}(\text{OH})_4^{2-}$ species becomes important in more basic conditions. The predominance fields of all of the ammonia-containing species decrease with decreasing nitrogen concentration and they become minor species at $[\text{N}]=10^{-6}$ M, while the simple chloride complexes expand at higher pH (similar to Fig. 9a).

In less saline solutions (Fig. 15b), the mixed ammonia–chloride complexes disappear, the simple Pt–hydroxide species increases in importance, and PtCl_3^- and $\text{Pt}(\text{NH}_3)\text{Cl}_5^-$ predominate in highly oxidizing acidic conditions. The predominance fields of all the ammonia species disappear if the N concentration is decreased by one order of magnitude, with hydroxide species occupying most of the Eh–pH space (similar to Fig. 9b).

The behaviour of Pd in aqueous solution in the presence of sulphur, hydroxide, ammonia and chloride is illustrated in Figure 16. Palladium sulphide compounds are the most stable species near the lower stability limit of water. The concentration of chloride ions determines the Pd(II)–chloride complex that is most stable in acidic oxidizing conditions. In highly saline

Fig. 17. Eh–pH diagrams for Rh in aqueous solution with $[\Sigma\text{Rh}]=10^{-9}$ M, $[\Sigma\text{S}]=10^{-3}$ M, $[\Sigma\text{N}]=5 \times 10^{-4}$ M and $[\Sigma\text{Cl}]=0.5$ M. Heavy solid lines separate stability fields of solid phases, light solid lines separate stability fields of aqueous species and dotted lines represent the stability limits of water.

solutions (Fig. 16a), PdCl_4^{2-} predominates at acidic pH, mixed ammonia–chloride complexes occur at pH ranging between 5 and 9 and the simple ammonia complex becomes important under more basic conditions. The predominance fields of the mixed complexes and the dissolved $\text{Pd}(\text{OH})_2(\text{aq})$ increase if the nitrogen concentration is decreased to 10^{-4} M and the simple ammonia species disappear. All of the mixed ammonia–chloride species disappear from the diagram for further decrease of $[\text{N}]$ to 10^{-6} M, while the predominance field of the simple chloride increases at a pH of ≈ 8 .

In less saline solutions (Fig. 16b), there are no mixed ammonia–chloride complexes, PdCl_3^- is the most stable chloride complex under acidic conditions, whereas the simple hydroxide and ammonium complexes predominate at higher pH; $\text{Pd}(\text{OH})_2(\text{aq})$ is the most important species in oxidizing conditions ($\text{Eh} > 0.5$) in the pH range between 3.5 and 6.5, and $\text{Pd}(\text{NH}_3)_4^{2+}$ predominates in basic conditions. The tetrammonium complex is unstable for $[\text{N}] < 2 \times 10^{-5}$ M.

The diagram for Rh (Fig. 17) does not change significantly as ligand concentrations change, apart from the transformations in the Rh–chloride species as described previously (Fig. 14). Near to the lower stability limit of water the Rh sulphide compound is the dominant species (Fig. 17). Rhodium hydroxide is likely to be the dominant inorganic species in oxidized surface waters at near-neutral and basic pH, whereas chloride complexes predominate under acidic oxidizing conditions.

DISCUSSION

The Eh–pH diagrams presented indicate that PGEs are able to form many thermodynamically stable complexes, including those of hydroxide, chloride, sulphide, ammonia and mixed ligand complexes, in the presence of these common inorganic ions. The significance of these PGE complexes depends upon the composition of fluids in the surface and near-surface environments. PGE hydroxide complexes (Figs. 1–3) may be the dominant inorganic species in oxidized surface waters such as lake and river water.

The results also suggest that PGEs emitted to the surface environment by VECs can react with sulphur species forming bisulphide complexes that could transport Pt and Pd in reducing environments (Figs. 4–6). The importance of sulphur species in the transport of PGEs has been demonstrated in a

study of Pt metabolization in plants (Klueppel *et al.* 1998) which showed that Pt is bound to sulphur by a mechanism involving sulphhydryl groups, for example by binding to a phytochelate (low molecular mass peptide). Moreover Pd(II) has been found to bind L-cysteine through interaction with sulphhydryl functional groups (Spikes & Hodgson 1969), and Nielson *et al.* (1985) also found indications of binding of Pd(II) to metallothionein.

The PGEs emitted by VECs may react with ammonia and there is evidence of the presence of ammonia in VEC gases. Ammonia emissions from catalyst-equipped vehicles have been shown by laboratory dynamometer studies to be much higher than for vehicles lacking catalysts (Cadle & Mulawa 1980). The on-road emission rate of ammonia from gasoline-powered vehicles was reported to be 1.3 ± 3.5 mg/km in 1981, when less than 10% of vehicles were equipped with three-way catalytic converters (Pierson & Brachavsek 1983). Fraser & Cass (1998) made measurements during 1993 when 76% of the fuel was consumed by three-way catalyst-equipped vehicles and found an average emission factor of 60 mg/km for ammonia. These results suggest that on-road vehicle ammonia emissions increased significantly following the introduction of three-way catalytic converters. Hence PGE-ammonium compounds may be important in mobilizing PGEs in the surface environments.

Chloride is a ubiquitous component of all natural waters (chloride concentrations up to 10^{-3} M and 0.8 M are found in freshwater and seawater, respectively). Also sodium chloride and calcium chloride are routinely used for snow and ice control on roadways. Elevated chloride concentrations have been reported during snowmelt conditions (Howard & Hayes 1997). Chloride is a highly soluble and mobile ion that does not biodegrade, volatilize or precipitate readily, nor does it absorb significantly on to mineral surfaces. Hence it is likely to travel through soil, enter groundwaters and eventually discharge into surface waters. Increased chloride levels in waters near roadways are a function of traffic patterns and road salting practices. Hence PGE-chloride complexes are likely to be formed in the roadside environment with the potential for significant quantities of Pt, Pd and Rh to be transported as chloride complexes. Indeed Nachtigall *et al.* (1996) found that Pt solubility in 0.9% NaCl is *c.* 18 times that of its solubility in pure water. Moreover, a study of the geochemical behaviour of naturally occurring Pt (Fuchs & Rose 1974) reported Pt mobility only in extremely acidic chloride-rich soils, possibly as a consequence of complex formation of divalent Pt, to form PtCl_4^{2-} .

Figure 18 represents the range of Eh–pH conditions in natural environments. The measured Eh values in waters in contact with the atmosphere, such as rainwater, streams, lakes and oceans are oxidizing, although bog waters and ground waters tend to be moderately reducing, because they are not in contact with atmospheric oxygen. Waterlogged, organic-rich soils, euxenic marine basins and organic-rich brines are even more reducing (Baas-Becking *et al.* 1960).

The environments in which the VEC-emitted PGEs are most likely dispersed are reported here with their inorganic ligand concentrations and Eh and pH values.

Road-runoff waters:

pH=4.0–9.5 (Mangani *et al.* 2005)
Eh=0.1–0.8 V (Baas-Becking *et al.* 1960)
[Cl]= 4×10^{-4} to 0.2 M (Mangani *et al.* 2005), 0.5 M for snowmelt conditions (Howard & Hayes 1997)
[NH₃]= 10^{-6} to 3×10^{-4} M (Agency for Toxic Substances & Disease Registry 2004a)
[H₂S/HS[−]/S^{2−}]= 10^{-6} to 10^{-3} M (Agency for Toxic Substances & Disease Registry 2004b; US Environmental Agency 2006)

Fig. 18. Range of Eh–pH conditions in natural environments. The dotted line represents the limit of the environment (after Baas-Becking *et al.* 1960).

Soil solutions:

pH=3.0–8.0 (Baas-Becking *et al.* 1960; Drever 1997)
Eh=0.1–0.75 V (for normal and wet soils. Wet soils are those subject to seasonal waterlogging but which may be quite dry at other times of the year) (Baas-Becking *et al.* 1960; Drever 1997)
[Cl]= 10^{-5} to 3×10^{-3} M (Drever 1997)
[NH₃]= 6×10^{-5} to 3×10^{-4} M (Agency for Toxic Substances & Disease Registry 2004a)
[H₂S/HS[−]/S^{2−}]= 10^{-6} to 4×10^{-4} M (Agency for Toxic Substances & Disease Registry 2004b)

Freshwater (not saline):

pH=4.0–8.5 (Baas-Becking *et al.* 1960; Stumm & Morgan 1996)
Eh=0.1–0.6 V (Baas-Becking *et al.* 1960)
[Cl]= 10^{-5} to 10^{-3} M (Stumm & Morgan 1996)
[NH₃]= 10^{-6} to 4×10^{-4} M (Agency for Toxic Substances & Disease Registry 2004a)
[H₂S/HS[−]/S^{2−}]= 10^{-6} to 10^{-4} M (Stumm & Morgan 1996; Agency for Toxic Substances & Disease Registry 2004b)

Seawater:

pH=7.5–8.5 (Baas-Becking *et al.* 1960; Stumm & Morgan 1996)
Eh=0.1–0.45 V (Baas-Becking *et al.* 1960)
[Cl]=0.5–0.8 M (Stumm & Morgan 1996)
[NH₃]= 10^{-6} to 10^{-4} M (Agency for Toxic Substances & Disease Registry 2004a)
[H₂S/HS[−]/S^{2−}]= 10^{-6} to 10^{-4} M (Agency for Toxic Substances & Disease Registry 2004b)

The hydroxide species of PGEs may be important in the transport of PGEs emitted by VECs in oxidizing surface environments with Eh–pH conditions similar to those of road-runoff waters, freshwater and soil solutions (Figs. 15b, 16b and 17). Bisulphide complexes are important at relatively low Eh values. The ammonia, chloride and hydroxide complexes are the species responsible for the mobility of Pt and Pd,

whereas chloride species are those mainly responsible for Rh solubility.

In highly saline solutions such as seawater ($7.5 < \text{pH} < 8.5$ and $0.1 < \text{Eh} < 0.45 \text{ V}$), ammonia and mixed ammonia–chloride complexes contribute the mobility of Pt and Pd respectively (Figs. 15a and 16a). However, for seawater having low ammonia concentration ($[\text{NH}_3] \approx 10^{-6} \text{ M}$), the Pt and Pd hydroxide and chloride species are important (Figs. 9a and 11a).

Road-runoff waters in snowmelt conditions are represented by Figures 15a, 16a and 17 and by Figures 9a, 11a and 13a for solutions having high ($5 \times 10^{-4} \text{ M}$) and low ammonia (10^{-6} M) concentrations, respectively. In the former situation (high ammonia concentration), mixed ammonium chloride species and simple chloride, ammonia and hydroxide species contribute to the transport of Pt and Pd, whereas chloride complexes are responsible for Rh mobility. In the latter situation (low ammonia concentration), only simple chloride and hydroxide species are important for the mobility of PGEs.

The Eh–pH diagrams also provide information on the behaviour of PGEs in the human body. The pH of the human stomach is ≈ 2 due to the presence of HCl. Under these conditions, metallic PGEs could be transformed into chloride salts, perhaps with increased health risks because of the toxicity of PGE–chloride complexes.

CONCLUSIONS

Thermodynamic calculations and physical chemical considerations suggest that Pt, Pd and Rh can form complexes with all the naturally occurring inorganic ions studied and that simple inorganic ligands have the capability to mobilize the PGEs through the formation of aqueous complexes. Sulphide compounds and bisulphide complexes are predominant in conditions of relatively low Eh, such as slightly oxidizing road-runoff waters, soil solutions and freshwater. The hydroxide species are likely to be important in the transport of PGEs in oxidizing environments such as road-runoff waters, freshwater, seawater and soil solutions, while ammonia may have a role in mobilizing the PGEs under near-neutral to basic, oxidizing conditions. Chloride species appear to be important under oxidizing, acidic and saline conditions, such as occur in road-runoff waters in snowmelt conditions and in highly acidic environments. Mixed ammonia–chloride species may also contribute to the transport of Pt and Pd in highly saline solutions such as seawater and road-runoff waters during snowmelt.

In view of the ever-increasing levels of PGEs in the environment due to VEC emissions, the evidence of their mobility and the well known toxicity of some PGE compounds, further investigations are required. In order to assess fully the ecotoxicological effects and health hazards of VEC-emitted PGEs, more detailed studies on their speciation and solubility under more realistic environmental conditions are necessary, as well as further investigations on PGE uptake and elimination patterns, bio-transformations and species inside living organisms. Identifying the source-pathway-targets of PGEs in the environment and the factors affecting their transport is important for managing risks from the future use of the platinum metals, especially in VECs.

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APPENDIX

Additional thermodynamic data used in the construction of the Eh–pH diagrams.

Substance	ΔG_f° (kcal/mol) at 25 °C and 1 bar	Ionic strength	Reference
Pt(OH) ⁺ (aq)	−2.15	0.1 M NaClO ₄	Wood <i>et al.</i> (1989)
Pt(OH) ₂ (aq)	−57.97	0.1 M NaClO ₄	Wood <i>et al.</i> (1989)
Pt(OH) ₃ [−] (aq)	−97.95	0.1 M NaClO ₄	Wood <i>et al.</i> (1989)
Pt(OH) ₄ ^{2−} (aq)	−140.26	0.1 M NaClO ₄	Wood <i>et al.</i> (1989)
Pt(HS) ₂ (aq)	−15.17	1 M NaClO ₄	Wood <i>et al.</i> (1994)
Pt(NH ₄) ₃ ²⁺ (aq)	−18.67	1 M NaClO ₄	Grinberg & Gel'fman (1961)
Pd(OH) ⁺ (aq)	−11.34	0.1 M NaClO ₄	Nabivanets & Kalabina (1970)
Pd(OH) ₂ (aq)	−65.15	0.1 M NaClO ₄	Nabivanets & Kalabina (1970)
Pd(OH) ₃ [−] (aq)	−105.19	0.1 M NaClO ₄	Nabivanets & Kalabina (1970)
Pd(OH) ₄ ^{2−} (aq)	−144.13	0.1 M NaClO ₄	Nabivanets & Kalabina (1970)
Pd(HS) ₂ (aq)	−12.32	1 M NaClO ₄	Wood <i>et al.</i> (1994)
Pd(NH ₄) ₃ ²⁺ (aq)	−27.58	1 M NaClO ₄	Rassmussen & Jorgensen (1968)
Rh(OH) ₃ (s)	−118.36	0.1M NaClO ₄	Forrester & Ayres (1959)
Rh(Cl) ⁺ (aq)	17.74	1 M NaClO ₄	Cozzi & Pantani (1958)
Rh(Cl) ₂ ⁺ (aq)	−16.53	1 M NaClO ₄	Cozzi & Pantani (1958)
Rh(Cl) ₃ (aq)	−49.78	1 M NaClO ₄	Cozzi & Pantani (1958)
Rh(Cl) ₄ [−] (aq)	−82.73	1 M NaClO ₄	Cozzi & Pantani (1958)
Rh(Cl) ₅ ^{2−} (aq)	−116.29	1 M NaClO ₄	Cozzi & Pantani (1958)
Rh(Cl) ₆ ^{3−} (aq)	−147.22	1 M NaClO ₄	Cozzi & Pantani (1958)

Free energy values were derived from published stability constant data by using NBS data for the ligands. The stability constant data are generally conditional, not thermodynamic, constants and so the derived free energy values in the table are also conditional.

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