

## The Chemistry of the Extraction of Gold

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### 15.1 General Principles

#### 15.1.1 The chemistry of gold compounds

Gold is the most noble of all the metals and this is the key to both its eternal romance and its many practical uses in industry. It is the only metal, for example, that is not attacked in air or water by either oxygen or sulphur, and its durability under the most corrosive conditions has led to its widespread use in coinage and jewellery through the ages.

Gold is the only metal that is generally found in nature in the metallic state, and the only gold compounds that occur in a natural state are the telluride and stibnite species,  $\text{AuTe}_2$  and  $\text{AuSb}_2$ . Gold reacts with all the halogens, most vigorously with bromine, which undergoes an exothermic reaction with gold powder at room temperature to produce  $\text{Au}_2\text{Br}_6$ .

Of greater importance to the extractive metallurgist is the chemistry of gold complexes in aqueous solutions, and this is a far broader subject. It has been traditionally accepted that gold complexes in aqueous solution can exist in one of two oxidation states, the aurous (+1) or the auric (+3), and that all the gold complexes of hydrometallurgical interest fall into these two groups. In more recent years, compounds with formal oxidation states of -1, +2, +4, and +5 have been prepared and identified (Puddephatt, 1978; Schutte, 1985), but these compounds are more of an academic curiosity at present and will not be dealt with in this review.

Thermodynamics predicts that neither aurous nor auric cations will be stable in aqueous solution, but will be reduced by water to metallic gold (see Section 15.1.2). In order to stabilize these ions in aqueous solutions, it is necessary to introduce a complexing ligand and to employ a suitable oxidizing agent, since no reaction occurs unless both are present in the solution. For example, gold does not dissolve in either nitric acid (an oxidizing agent) or hydrochloric acid (a complexing ligand), but dissolves quite easily in a mixture of the two, aqua regia. Whether they are solid, in solution, or in the gaseous state, gold compounds are invariably bound covalently, and by far the majority are complexes.\*

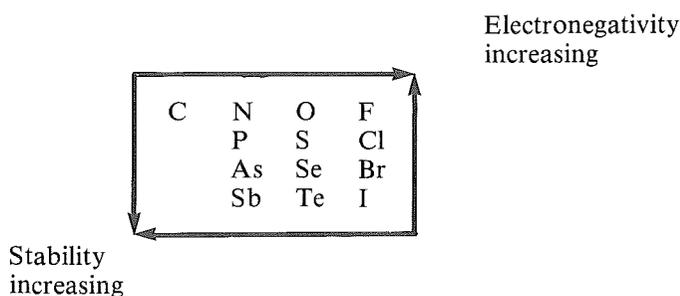
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\*NOMENCLATURE: A *complex* consists of a central cation with a number of ligands bonded to it. *Ligands* may be ions (e.g.  $\text{Cl}^-$ ,  $\text{SCN}^-$ ) or uncharged molecules (e.g.  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $(\text{NH}_2)_2\text{CS}$ ). The number of ligands bonded to the cation is known as the *co-ordination number* of the cation. The *stability constant*  $\beta_n$  of a complex formed

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A glance at any chemistry text shows that there are a large number of gold complexes with a wide range of stabilities. Generalizations can be made to show that the properties of these complexes vary systematically. These allow many of the known thermodynamic characteristics of gold complexes to be rationalized, and provide some basis for the prediction of their behaviour.

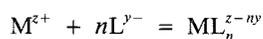
A useful first generalization about the stability of gold complexes relates to the nature of the ligand donor atom, i.e. the atom in the ligand that is bonded directly to the gold. Both gold(I) and gold(III) are B-type metal ions, which means that the stability of their complexes tends to decrease as the electronegativity of the ligand donor atom increases (i.e. as the tendency of the atom to attract electrons increases). This leads to stability orders such as  $I^- > Br^- > Cl^- > F^-$ , where the order of electronegativities is  $F^- > Cl^- > Br^- > I^-$ . More generally, it is apparent that electronegativity is a periodic property of the elements, and for elements that would possibly form complexes with gold, there is the following scheme:



This scheme accounts for the stability orders noted above for halogen complexes. It also accounts for stability orders such as  $\underline{Se}CN^- > \underline{S}CN^- > \underline{O}CN^-$  or  $\underline{CN}^- > \underline{NH}_3 > \underline{H}_2O$  (the atom bonded to gold is underlined in each case), and suggests why gold tellurides and stibnites are stable enough to be found in nature.

For more accurate prediction of the stability of gold complexes it is

from a cation,  $M^{z+}$ , and  $n$  ligands,  $L^{y-}$ , is the *equilibrium constant* of the reaction for its formation from the free cation and ligands:



$$\beta_n = \frac{[ML_n^{z-ny}]}{[M^{z+}] [L^{y-}]^n}$$

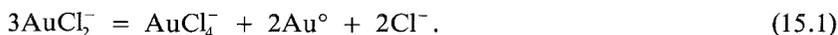
[ ] denotes the *activity* of the species enclosed. If conditions are such that  $ML_n^{z-ny}$  precipitates from solution, the relationship

$$K_s = [M^{z+}] [L^{y-}]^n$$

holds.  $K_s$  is known as the *solubility product*.

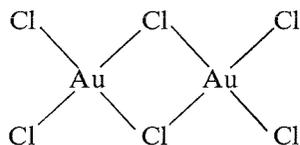
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necessary to take this argument a step further. In general, whether the oxidation of gold to the complex  $\text{AuL}_2^+$  or  $\text{AuL}_4^{3+}$  occurs in the presence of a particular ligand depends on the strength of the oxidizing agent and on the relative standard reduction potentials for the reduction of gold(I) or gold(III) to the metal in the presence of the particular ligand. It is also apparent that the requirements for complex stability are different for gold(I) and gold(III) (Finkelstein and Hancock, 1974), with less electronegative or 'soft' donor atoms preferring metal ions of low valency, and 'hard' donor atoms preferring metal ions of high valency. Therefore gold(I) forms more stable complexes with ligands containing soft donor atoms such as S, C, Se, and P, while gold(III) forms more stable complexes with the more electronegative, or hard, donor atoms such as N, O, F, Cl, etc. This indicates that complexes of gold(III) with soft ligands will be easily reduced to the gold(I) state, while complexes of gold(I) with hard donor ligands will probably disproportionate to gold(III) and gold (0). This accounts for the fact that gold(I) preferentially forms aurous complexes with ligands such as cyanide, thiourea, thiocyanate, and thiosulphate (which all have soft donor atoms) whereas, in chloride solution (hard donor atom), the monovalent  $\text{AuCl}_2^-$  species tends to disproportionate according to the following reaction:



Gold(I) has the closed shell  $4f^{14}5d^{10}$  electronic configuration, and therefore gold(I) complexes are diamagnetic and adopt regular structures. All known gold(III) complexes have the low-spin  $4f^{14}5d^8$  electronic configuration and are also diamagnetic.

The preferred co-ordination number of gold(I) is 2 and that of gold(III) is 4, with gold(I) tending to form linear complexes and gold(III) tending to form square planar complexes. For example, the cyanide complexes of gold(I) and gold(III) are  $\text{Au}(\text{CN})_2^-$  and  $\text{Au}(\text{CN})_4^-$ , respectively, and both gold(I) and gold(III) tend to take up extra ligands in an effort to attain their preferred co-ordination numbers. Thus insoluble AuCN in contact with a solution containing cyanide ions will tend to take up a second  $\text{CN}^-$  to form the soluble  $\text{Au}(\text{CN})_2^-$ , whereas AuCN in the solid state attains the required co-ordination number by forming a polymer of the type . . .  $\text{Au}-\text{C}\equiv\text{N}-\text{Au}-\text{C}\equiv\text{N}$ . . . When additional cyanide is available, however,  $\text{Au}(\text{CN})_2^-$  is preferred to polymeric AuCN because the Au-C bond is stronger than the Au-N bond in the polymer. Similarly, compounds such as  $\text{AuCl}_3$  form dimers in the solid or gaseous states to satisfy the co-ordination number of 4 required by gold(III):



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Table 15.1. Stability constants\* for a selection of complexes of gold(I) and gold(III).

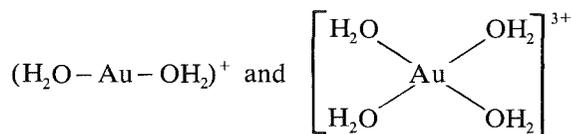
Gold(I)		Gold(III)	
Complex	$\beta_2$	Complex	$\beta_4$
$\text{Au}(\text{CN})_2^-$	$2 \times 10^{38}\ddagger$	$\text{Au}(\text{CN})_4^-$	$\sim 10^{56}$
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	$5 \times 10^{28}$	$\text{AuI}_4^-$	$5 \times 10^{47}$
$\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$	$2 \times 10^{23}\ddagger$	$\text{Au}(\text{SCN})_4^-$	$10^{42}$
$\text{AuI}_2^-$	$4 \times 10^{19}$	$\text{AuBr}_4^-$	$10^{32}$
$\text{Au}(\text{SCN})_2^-$	$1,3 \times 10^{17}$	$\text{AuCl}_4^-$	$10^{26}$
$\text{AuBr}_2^-$	$10^{12}$		
$\text{AuCl}_2^-$	$10^9$		

\*Values of stability constants used in this chapter are taken from the tabulations of Sillen (Sillen and Martell, 1964) unless otherwise indicated.

‡Hancock and Finkelstein (1970).

†Calculated from standard reduction-potential data reported by Groenewald (1975).

It should be noted that, although aurous and auric ions are generally represented as  $\text{Au}^+$  and  $\text{Au}^{3+}$ , they do not occur in solution as the bare ions, but in a hydrated state as complexes containing the number of water molecules appropriate to the co-ordination requirements of the particular oxidation state:



Since the atom bound to the gold in each of these ions is oxygen, these complexes are of low stability. (Oxygen occurs at the top and towards the right of the partial periodic table shown previously.) The simple ions tend to react in solution to replace the water molecules by stronger ligands. Similarly, if  $\text{AuCl}_3$  is dissolved in water, it does not (as the chlorides of many other cations do) give rise to a free hydrated ion and free chloride. Instead, the chlorides remain bound to the gold, and dimerization takes place to satisfy the co-ordination number requirements. If another ligand is present in solution, the dimer breaks down and the ligand takes up the vacant co-ordination position.

The gold(I) and gold(III) compounds that are of the greatest importance to the extractive metallurgist are listed in Table 15.1, which also provides information on the co-ordination numbers and stabilities of these complexes.

The gold(I) complex of greatest importance to the extractive metallurgist is undoubtedly the extremely stable aurocyanide anion, which, for the reasons outlined above, is the predominant gold species present in cyanide leach liquors. There is no evidence for the formation of species with co-ordination numbers greater than 2, analogous to the copper(I) complex anions

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$\text{Cu}(\text{CN})_3^{2-}$  and  $\text{Cu}(\text{CN})_4^{3-}$ . The insoluble gold cyanide compound  $\text{AuCN}$  precipitates from acidic solutions of aurocyanide ions as follows:



This reaction takes place readily in strongly acidic solution and slowly in weak acid solutions (pH 2 to 3). The reaction is of significance on South African gold plants where uranium and gold are recovered from the same milled ore. Uranium is leached in acidic solution (pH 1 to 2), and any aurocyanide present in solution in the feed to the uranium-leaching plant will precipitate as  $\text{AuCN}$ , and will be lost with the solid residue from the plant. This has been a major impediment to the development of processes for the simultaneous leaching of gold and uranium, which would have obvious economic advantages over the conventional two-stage process.

The aurocyanide anion is readily oxidized by halogens to mixed-ligand auric complexes of the type  $[\text{Au}(\text{CN})_2\text{X}_2]^-$  (where X is  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ ). Other cyanide complexes include the thallium(I) salt  $\text{Tl}[\text{Au}(\text{CN})_2]$ , in which there is evidence of interaction between Tl and Au (Stammreich *et al.*, 1968), the linear neutral molecule  $\text{AuCN}(\text{PPh}_3)$  (Cariati *et al.*, 1970), and the complex  $\text{Au}(\text{PPh}_3)_3 \text{Au}(\text{CN})_2$ , in which both cationic and anionic gold(I) species are present (Cariati *et al.*, 1970). Gold-cyanide-phosphine complexes have been extensively studied, and were last reviewed in 1974 (Rigo and Turco, 1974).

Other complex aurous ions that are relevant in hydrometallurgy are the thiourea, thiosulphate, and thiocyanate complexes. These are the only ligands that are likely to compete with cyanide in the large-scale processing of gold ores, and they are likely to become more important, since increased attention is being focused on the search for alternatives to the environmentally undesirable cyanide process. The thiourea complex is unique in that it is the only cation amongst the complexes listed in Table 15.1, and this paves the way to novel process options for the extraction of gold from thiourea leach liquor (Groenewald, 1977).

The extensive chemistry of gold(I) complexes is almost matched by that of gold(III) complexes, the vast majority of which have 4-co-ordinate square planar stereochemistry. Examples include the complex anion  $\text{AuCl}_4^-$  and the cation  $\text{Au}(\text{NH}_3)_4^{3+}$ , but the simple aquo-ion  $\text{Au}(\text{H}_2\text{O})_4^{3+}$  is not formed in measurable concentration, even when gold(III) hydroxide is dissolved in nitric or sulphuric acid (Bezzubenko and Peshchevskii, 1962). All auric complexes are strong oxidizing agents.

The halides are the most important gold(III) complexes from a hydrometallurgical point of view. Gold dissolves readily in aqueous chloride solution in the presence of an appropriate oxidizing agent (such as chlorine, nitric acid, or ferric ions) to form the tetrachloroauric ion. This ion can be isolated as a hydrated acid, such as  $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$ , by evaporation of the solution, or as a salt such as  $\text{Na}[\text{AuCl}_4]$ . Tetrafluoro and tetrabromo complexes of gold(III) are also stable in aqueous solution, but salts of the  $\text{AuI}_4^-$  ion cannot be prepared from aqueous solution, since partial reduction to  $\text{AuI}_2^-$  takes place. Halide complexes of mixed valency such as

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$\text{Cs}_2[\text{AuCl}_2][\text{AuCl}_4]$  are also known. In aqueous solution both the  $\text{AuCl}_4^-$  and  $\text{AuBr}_4^-$  ions are hydrolysed to some extent, forming species such as  $[\text{AuCl}_3]\text{H}_2\text{O}$  and  $[\text{AuBr}_3]\text{H}_2\text{O}$ . These in turn act as weak acids forming species such as  $\text{AuX}_{4-n}(\text{OH})_n$  (where X is Cl, Br, or I, and  $n = 0$  to 4 with increasing alkalinity) in alkaline solution. The species  $\text{Au}(\text{OH})_4$  is stable in strongly alkaline solution.

The auricyanide complex,  $\text{Au}(\text{CN})_4^-$ , like the corresponding aurous complex, is extremely stable, its stability constant, which is known only approximately, being of the order of  $10^{56}$ . The complex  $\text{K}[\text{Au}(\text{CN})_4]$  is prepared by the addition of a solution of  $\text{Na}[\text{AuCl}_4]$  to a concentrated potassium cyanide solution, and complex anions of higher co-ordination number, such as  $\text{Au}(\text{CN})_5^{2-}$  and  $\text{Au}(\text{CN})_6^{3-}$ , are formed in solutions containing excess cyanide.

A great many other gold(I) and gold(III) compounds have been prepared and identified, mostly in the last 10 to 20 years. The most numerous are the multitude of phosphine, arsine, and stibine complexes that tend to dominate gold(I) chemistry. Gold(III), being a harder Lewis acid than gold(I), not only forms complexes readily with soft ligands, but also with hard ligands such as fluoride and nitrogen donors. Some of these compounds may undergo reactions of importance to the hydrometallurgist, and interested readers are referred to the recent reviews of Puddephatt (1978) and Schutte (1985).

### 15.1.2 An equilibrium approach to the hydrometallurgy of gold

Any chemical reaction, such as the reduction of a metal ion  $\text{M}^{2+}$  with hydrogen



has a thermodynamic driving force, the Gibbs free energy change of reaction,  $\Delta G$ . The value of  $\Delta G$  is determined by the reacting species, their activities, the temperature, and the pressure. If  $\Delta G$  is zero, the reaction is at equilibrium. If  $\Delta G$  has a negative value, the reaction is driven in the forward direction and reduction of the metal ions occurs, resulting in a decrease in the activities of the reactants and an increase in the activities of the products with a corresponding decrease in the absolute value of  $\Delta G$ , i.e. the reaction moves towards equilibrium. If  $\Delta G$  has a positive value, the reaction is driven in the reverse direction, resulting in the oxidation of M to  $\text{M}^{2+}$ , and a similar decrease in the absolute value of  $\Delta G$ .

The rate at which the reaction moves towards equilibrium is dependent on a number of additional parameters that will not be discussed in this section. It is important to note, however, that the rate of reaction is only indirectly affected by the absolute value of  $\Delta G$ .

Reaction (15.3) can be considered to represent a galvanic cell consisting of the two half-cell reactions:



and



The electromotive force of the cell,  $E$ , is defined by the equation

$$E = -\Delta G/nF, \quad (15.6)$$

where  $n$  is the stoichiometric number of electrons involved in the reaction (2 in this case), and  $F$  is the Faraday constant ( $96\,487\text{ C mol}^{-1}$ ). Under standard conditions of  $25^\circ\text{C}$ ,  $100\text{ kPa}$ , and unit activities of all reacting species, Equation (15.6) can be written as

$$E^\circ = -\Delta G^\circ/nF, \quad (15.7)$$

where  $E^\circ$  and  $\Delta G^\circ$  are the standard potential and the standard Gibbs free-energy change of reaction (15.3) respectively.

The relationship between  $E$  and  $E^\circ$  is given by the Nernst equation:

$$E = E^\circ - (RT/nF) \ln K, \quad (15.8)$$

where  $R$  is the universal gas constant ( $8,314\text{ J K}^{-1}\text{ mol}^{-1}$ ),  $T$  is absolute temperature, and  $K$  is the equilibrium constant. At  $25^\circ\text{C}$  the constants in Equation (15.8) can be evaluated, yielding

$$E = E^\circ - \frac{0,0591}{n} \log K. \quad (15.9)$$

$K$  is defined as the arithmetic product of the activities of the reaction products raised to their stoichiometric numbers divided by the arithmetic product of the activities of the reacting species raised to their stoichiometric numbers. If the concentrations of all the reacting species are below about  $0,01\text{ mol l}^{-1}$ , the activity coefficients are generally close to unity, and the activities can be replaced by concentrations with little error. If the concentrations are high, the error introduced into the potentials can be as large as  $50\text{ mV}$ . Because of the difficulties that are encountered in the determination of activities, this discussion will, for the sake of simplicity, approximate all activities by concentrations, and any possible errors incurred will be ignored.

In order that the Nernst equation can be applicable to half-cell reactions such as that described by Equation (15.4), a reference half-cell must be defined. This reference is taken to be the hydrogen reaction, (15.5), for which both  $\Delta G^\circ$  and  $E^\circ$  are assumed to be zero. The activity of all solid phases is defined as unity, and the Gibbs free energy of all pure elements in their standard states is set to zero. Under these conditions, the free-energy change for a reaction can be calculated from tabulated values of the standard Gibbs free energy of formation,  $\Delta G_f^\circ$ , for all the reacting species.

In a reaction such as



the standard Gibbs free-energy change for the reaction,  $\Delta G^\circ$ , is given by

$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{Au}) - \Delta G_f^\circ(\text{Au}^{3+}) \\ &= -433\text{ kJ mol}^{-1}. \end{aligned} \quad (15.11)$$

(Unless stated otherwise, all free-energy data were obtained from Pourbaix, 1966 or Wagman *et al.*, 1965.) The standard reduction potential for Equation (15.10) is therefore

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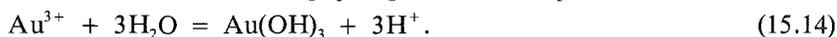
$$\begin{aligned} E^\circ &= 433 \times 10^3 / (3 \times 96\,487) \text{ V} \\ &= 1,50 \text{ V} \end{aligned} \quad (15.12)$$

The large positive value of  $E^\circ$  (or the large negative value of  $\Delta G^\circ$ ) indicates that  $\text{Au}^{3+}$  is thermodynamically unstable, and should be readily reduced to Au. With a value of  $-237 \text{ kJ mol}^{-1}$  for the Gibbs free energy of water, the standard reduction potential for the reaction



is 1,23 V. Because this value is lower than the value of 1,50 V for the  $\text{Au}^{3+} - \text{Au}$  reaction,  $\text{Au}^{3+}$  is unstable in water, and will undergo spontaneous reduction to Au with the oxidation of water to oxygen. It can also be concluded that oxygen, with a standard reduction potential of 1,23 V, is not able to oxidize Au to  $\text{Au}^{3+}$ .

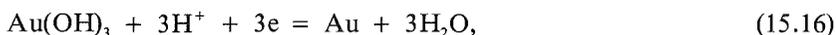
With increasing pH of the electrolyte, the  $\text{Au}^{3+}$  ion will be precipitated as hydrated auric oxide,  $\text{Au}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  or  $\text{Au}(\text{OH})_3$ , i.e.



When reaction (15.14) has attained equilibrium,  $\Delta G = 0$ , and hence

$$\Delta G^\circ = -RT \ln([\text{H}^+]^3 / [\text{Au}^{3+}]), \quad (15.15)$$

from which it can be shown that  $\text{Au}^{3+}$  of unit activity is at equilibrium with solid  $\text{Au}(\text{OH})_3$  at a pH value of  $-0,3$ . The reduction of  $\text{Au}(\text{OH})_3$  to Au,



can be shown to have a standard reduction potential of 1,48 V, and hence the reduction potential at any pH value will be expressed by the equation

$$E = 1,48 - 0,0591 \text{ pH} \quad (15.17)$$

The reduction of  $\text{Au}^{3+}$  to Au (15.10), the precipitation of  $\text{Au}^{3+}$  as  $\text{Au}(\text{OH})_3$  (15.14), and the reduction of  $\text{Au}(\text{OH})_3$  to Au (15.16) are examples of three distinct classes of reaction, viz.

- i) dependent on potential, but independent of pH,
- ii) independent of potential, but dependent on pH, and
- iii) dependent on potential, and dependent on pH.

Values of the Gibbs free energies can be found for a number of gold compounds in the compilations cited above. Equations representing reactions between these compounds can be written, and the potentials and critical pH values that correspond to these reactions can be calculated from the free energies. For the meaningful interpretation of this large amount of data, it is convenient to plot the data in the form of a potential – pH diagram (also referred to as a Pourbaix diagram), as shown in Figure 15.1. Equations of class (i) above appear as horizontal lines, those of class (ii) as vertical lines, and those of class (iii) as lines angled above or below the horizontal. Solid phases are indicated by bold print, and soluble aqueous species by light print.

The potential – pH diagram in Figure 15.1, which represents the reactions of gold in the absence of any complexing agents, shows only the major reactions. A complete diagram can be found in Pourbaix (1966). The two

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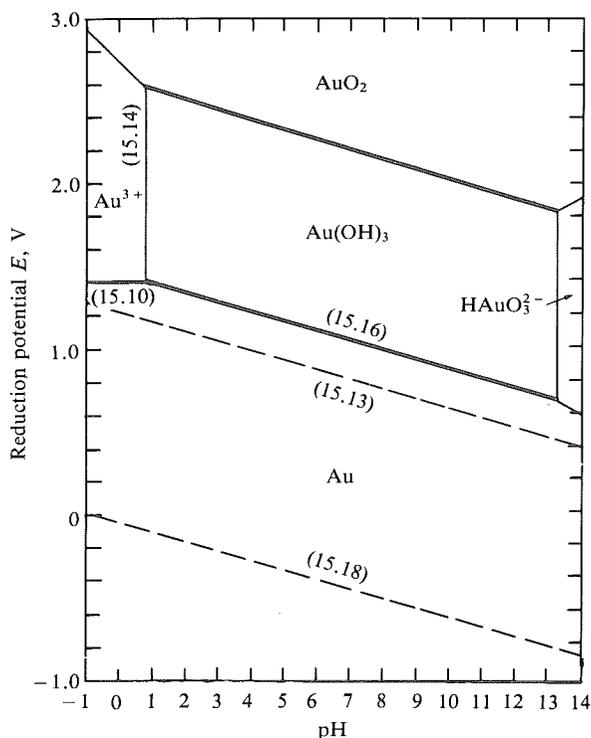


Figure 15.1. Potential-pH equilibrium diagram for the system Au-H<sub>2</sub>O at 25°C. The labels on the lines refer to the equation numbers in the text. Concentrations of all soluble gold species are 10<sup>-4</sup> M. P<sub>O<sub>2</sub></sub> = 1 atm. = P<sub>H<sub>2</sub></sub> (after Adamson, 1972).

dashed lines refer to the reduction of water,



at  $E = -0,0591 \text{ pH}$ ,

and to the reduction of oxygen,



at  $E = 1,23 - 0,0591 \text{ pH}$ .

(The fugacities of H<sub>2</sub> and O<sub>2</sub> are assumed to be unity.)

The extremely large stability domain of metallic gold, which extends above the O<sub>2</sub>-H<sub>2</sub>O line, indicates that gold is stable with respect to oxidation by oxygen at all pH values, including those of the halogen mineral acids, sulphuric, nitric, and phosphoric acids, and caustic alkalis.

In the presence of strong complexing agents, which can stabilize gold in either the +1 or +3 oxidation states, the potential-pH diagram can be significantly affected. As an example, the effect of cyanide ions on the reaction

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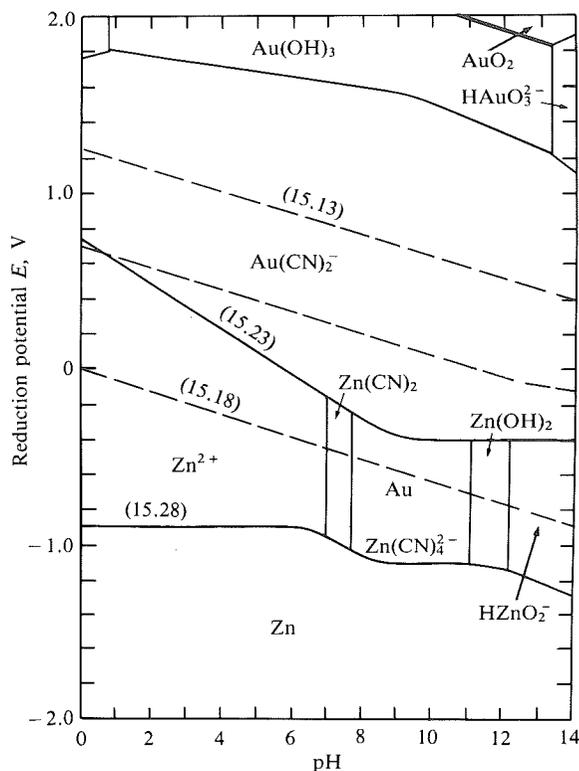
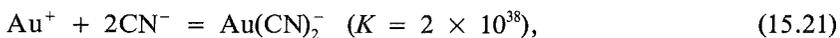


Figure 15.2. Potential-pH equilibrium diagram illustrating features of the Au-CN-H<sub>2</sub>O and Zn-CN-H<sub>2</sub>O systems at 25°C.  $[CN^-]_{total} = 10^{-3} \text{ mol l}^{-1}$ ,  $[Au(CN)_2^-] = 10^{-4} \text{ mol l}^{-1}$ ,  $[Zn^{2+}]_{total} = 10^{-3} \text{ mol l}^{-1}$ .



$$E = 1,69 - 0,0591 \log [Au^+] \tag{15.20}$$

is considered. Because of the strong complex between Au<sup>+</sup> and CN<sup>-</sup>, viz.



Equation (15.20) can be rewritten as

$$E = 1,69 - 0,0591 \log K - 0,0591 \log ([CN^-]^2/[Au(CN)_2^-]), \tag{15.22}$$

which results in a negative shift in the  $E^0$  value from 1,69 V to -0,57 V. This lower  $E^0$  value applies to the new reaction obtained when Equations (15.21) and (15.19) are added:



Because HCN is a weak acid (the dissociation constant for the reaction



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is  $4,93 \times 10^{-10}$ ), a lowering of pH results in a reduction in the concentration of free cyanide ions. The effect of this hydrolysis reaction can be incorporated into Equation (15.22), yielding

$$E = 0,53 + 0,059 \log [\text{Au}(\text{CN})_2^-] - 0,118 \log ([\text{CN}]_{\text{tot}} - 2 [\text{Au}(\text{CN})_2^-]) + 0,118 \log (4,93 \times 10^{-10} + [\text{H}^+]), \quad (15.25)$$

where  $[\text{CN}]_{\text{tot}}$  is the total concentration of cyanide added to the solution. Equation (15.25) represents the relationship between the reduction potential for (15.23) and the concentrations of all the species that may affect the value of  $E$ .

The potentials corresponding to Equation (15.25) are shown in Figure 15.2. Because of the strong stabilizing effect of the cyanide ion, metallic gold will be readily oxidized to aurocyanide ions by dissolved oxygen. It is of interest to note, however, that the reduction of oxygen on a gold surface in an electrolyte containing cyanide ions can yield an appreciable amount of hydrogen peroxide (Habashi, 1966), cf. Section 15.1.3.3.



$$E = 0,682 - 0,0591 \text{ pH} \quad (15.27)$$

rather than proceeding to water (15.13). Fortunately, the negative shift in the equilibrium potential for gold in the presence of cyanide ions still remains positive with respect to the reduction potential of zinc in the same electrolyte. Zinc ions form fairly strong complexes with both  $\text{OH}^-$  and  $\text{CN}^-$ , forming numerous compounds such as  $\text{ZnOH}^+$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{HZnO}_2^-$ ,  $\text{ZnO}_2^{2-}$  and  $\text{Zn}(\text{CN})_x^{2-x}$ , where  $x$  is from 1 to 4 (Finkelstein, 1972; Osseo-Asare *et al.*, 1984a). The effect of these complexes is to shift the reduction potential of the reaction



$$E = -0,76 + 0,0295 \log [\text{Zn}^{2+}] \quad (15.29)$$

to slightly more negative values at pH values above 7. The potentials corresponding to the reduction of zinc are shown in Figure 15.2, from which it is evident that dissolved aurocyanide ions will be reduced to metallic gold by the corresponding oxidation of zinc.

It is of importance to note that the reduction potentials of zinc are below those for both the reduction of oxygen (15.13) and water (15.18). Zinc is rapidly oxidized by dissolved oxygen, and hence one needs to deaerate the electrolyte prior to cementation in order to reduce the consumption of zinc. However, zinc will still corrode spontaneously in water as hydrogen is evolved, which accounts for the large stoichiometric excess of zinc required for the cementation of gold.

Inspection of the electrochemical series reveals two further reduction reactions that could be used for the precipitation of gold from cyanide, viz. those of aluminium and borohydride:



$$E = -1,26 - 0,0788 \text{ pH} + 0,0197 \log [\text{AlO}_2^-], \quad (15.31)$$

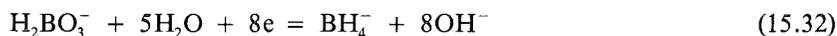
## THE EXTRACTIVE METALLURGY OF GOLD

Table 15.2. Standard reduction potentials for various reactions of gold (after Schmid and Curley-Fiorino, 1975).

Reaction	$E^\circ$ (V)
$\text{Au}^+ + e = \text{Au}$	1,69
$\text{AuCl}_2^- + e = \text{Au} + 2\text{Cl}^-$	1,154
$\text{Au}(\text{SCN})_2^- + e = \text{Au} + 2\text{SCN}^-$	0,662
$\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+ + e = \text{Au} + 2\text{CS}(\text{NH}_2)_2$	0,352*
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-} + e = \text{Au} + 2\text{S}_2\text{O}_3^{2-}$	0,15
$\text{Au}(\text{CN})_2^- + e = \text{Au} + 2\text{CN}^-$	-0,57
$\text{Au}^{3+} + 3e = \text{Au}$	1,50
$\text{AuCl}_4^- + 3e = \text{Au} + 4\text{Cl}^-$	1,002
$\text{Au}(\text{SCN})_4^- + 3e = \text{Au} + 4\text{SCN}^-$	0,623
$\text{Au}^{3+} + 2e = \text{Au}^+$	1,40
$\text{Au}(\text{SCN})_4^- + 2e = \text{Au}(\text{SCN})_2^- + 2\text{SCN}^-$	0,604
$\text{AuCl}_4^- + 2e = \text{AuCl}_2^- + 2\text{Cl}^-$	0,926

\*Groenewald (1977)

and



$$E = -0,413 - 0,0591 \text{ pH} + 0,0074 \log \left( \frac{[\text{H}_2\text{BO}_3^-]}{[\text{BH}_4^-]} \right). \quad (15.33)$$

However, because the reduction potentials of these reactions at a pH of 11 ( $-2,13$  V and  $-1,06$  V respectively) are very negative compared to that for the reduction of water ( $-0,65$  V), the consumption of reagent due to the evolution of hydrogen is high.

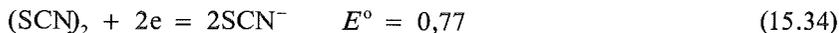
The hydrometallurgy of gold is not confined entirely to that of the cyanide system, since gold also forms strong complexes with a number of other ligands such as thiourea, thiosulphate, thiocyanate, and chloride. The standard reduction potentials for these reactions are shown in Table 15.2.

The effect of chloride ions on the potential-pH behaviour of gold has been discussed in detail by Finkelstein (1972). It is evident from the potentials in Table 15.2 that the stable oxidation state of gold in the presence of chloride ions is +3. The reduction potential for auric chloride (1,002 V) is below that for the reduction of oxygen to water (1,23 V), and hence it would appear that gold should be dissolved by oxygen in strong chloride electrolytes. The rate of oxidation is extremely low, so that gold appears to be inert under such conditions. In practice, stronger oxidants such as dissolved chlorine ( $E^\circ = 1,395$  V) or hypochlorite ( $E^\circ = 1,715$  V) are used for the oxidation of metallic gold. Solutions of auric chloride are readily reduced to metallic gold by soluble reductants such as sulphite, nitrite, ferrous, and stannous ions.

Gold is stable in the +3 oxidation state in electrolytes containing unit activities of dissolved gold and thiocyanate ions. However, the equilibrium potential is shifted negatively as the concentration of dissolved gold is decreased, and this shift is greater by a factor of 3 for gold in the +1 oxidation state. As a result of this shift, gold in the +1 oxidation state becomes the stable species when the logarithm of the concentration of dissolved gold falls

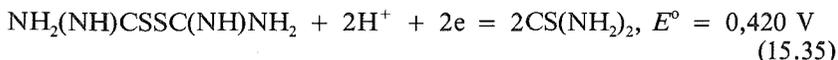
below  $-0,98 + \log[\text{SCN}^-]$ , i.e. when the concentration of gold is less than 0,1 of the thiocyanate concentration.

Gold in the presence of thiocyanate ions is thermodynamically unstable in the presence of oxidizing agents such as  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ , and  $\text{Fe}^{3+}$ . It should, however, be noted that thiocyanate ions can be oxidized to thiocyanogen according to the reaction (Latimer, 1952):



Very strong oxidants, such as hydrogen peroxide, may therefore destroy the complexing ligand, resulting in poor dissolution of the gold.

The neutral ligand thiourea forms a strong complex with  $\text{Au}^+$ , thereby forming a soluble gold compound exhibiting a positive charge. Because of the low  $E^\circ$  value (0,352 V) of the gold-thiourea complex, gold is readily oxidized in the presence of thiourea. However, thiourea is readily oxidized to formamidine disulphide (Preisler and Berger, 1947):



so that a marked loss of thiourea would be expected even in the presence of  $\text{Fe}^{3+}$  ( $E^\circ = 0,77 \text{ V}$ ). The stability of thiourea towards oxidation is reduced with increasing pH.

Thiosulphate co-ordinates strongly with  $\text{Au}^+$ , yielding a standard reduction potential of 0,15 V. Unfortunately, thiosulphate is unstable in acidic as well as alkaline environments and will be oxidized to tetrathionate, sulphite or sulphate.

### 15.1.3 Electrochemical aspects

The thermodynamic characteristics of gold and its compounds of relevance to the hydrometallurgy of gold have been outlined above. Of perhaps greater importance are the kinetic considerations that apply to the leaching and precipitation of gold. As will be discussed in detail in the next section, both of these processes are electrochemical in nature, and it is therefore of some importance that the electrochemistry of these systems should be briefly reviewed as it pertains to these processes. The dissolution of gold involves an oxidative (or in an electrochemical sense, anodic) reaction, whereas its precipitation by cementation requires a reductive (or cathodic) process. Each of these will be discussed in turn.

#### 15.1.3.1 Anodic reactions of gold

The electrochemical behaviour of the noble metals (the platinum-group metals plus gold) under oxidizing conditions is dominated by the formation of oxide films. This can have pronounced effects on the kinetics of dissolution of these metals, and partly accounts for their refractory nature. In the case of gold, the nature and kinetics of formation of oxide films have been extensively studied (Nicol, 1980a) and, while the results have shown that the oxidation processes are complex, the important overall characteristics in acidic and alkaline solutions can be demonstrated by the data in Figure 15.3. In these experiments, the current flowing at a gold electrode in the solution

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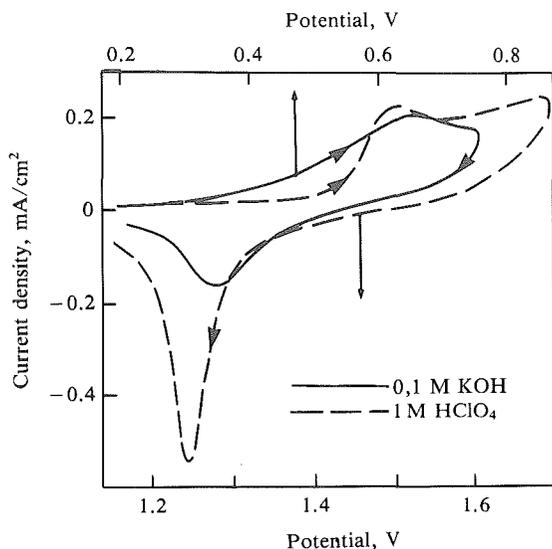


Figure 15.3. Cyclic voltammograms for the oxidation of gold in 0,1 M potassium hydroxide and in 1 M perchloric acid. The abscissa scales are of different sensitivities as well as laterally displaced to allow the curves to overlap and to demonstrate their general similarity (after Nicol, 1980b).

shown was measured, and the potential was first increased and then decreased. Positive currents correspond to anodic reactions, and negative currents to cathodic reactions. The oxidation of gold therefore begins at about 1,4 V in acidic solutions, and at 0,4 V in alkaline solutions. The peaks at 1,25 V and 0,35 V on the reverse sweeps are due to the reduction of the oxide films back to the metal.

These observations imply that the formation of oxide films can be expected to adversely affect the dissolution of gold at potentials above 0,4 V in alkaline solutions and 1,4 V in acidic solutions.

In the presence of species (or ligands) that form complexes with gold in solution, the anodic characteristics of gold can be significantly modified as a result of the increased stability of the gold(I) or gold(III) complexes with the ligands. Of these, only the behaviour in chloride, thiourea, and cyanide solutions has been studied in any detail, and the major conclusions of the published work will be summarized below, particularly where they relate to the use of these ligands in the extraction and refining of gold.

### (a) Chloride

The main features of the anodic behaviour of gold in acidic chloride solutions are shown in Figure 15.4, from which it can be seen that dissolution occurs at potentials above about 1 V. The plateau at high current densities is due to the limited rate of mass transport of chloride to the gold surface,

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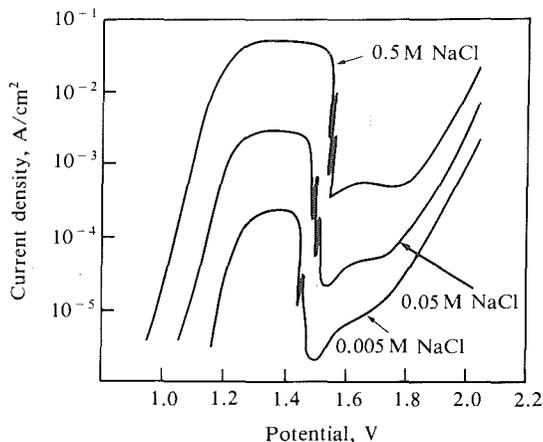
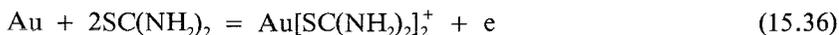


Figure 15.4 Steady-state current versus potential curves for the oxidation of gold in solutions containing 0.5 M sulphuric acid and various amounts of chloride (after Heumann and Panesar, 1966).

while the rapid decrease in the rate of dissolution from 1.4 to 1.5 V is due to passivation of the surface by oxide, as predicted from the curve for acidic solutions in Figure 15.3. Dissolution in the active region (i.e. at potential below 1.4 V) is complex in that, depending on a number of variables such as chloride concentration, temperature, and degree of agitation, both gold(I) and gold(III) can be formed in varying proportions. Work at the Council for Mineral Technology (Mintek) reported by Nicol and Schalch (1976b) demonstrated that the formation of gold(I) at the anodes of the chloride-based electrorefining process can lead to a number of operational problems in the refining of gold. Some aspects of this will be discussed in Section 15.1.3.3(c).

### (b) Thiourea

Gold(I) forms the strong cationic complex  $\text{Au}[\text{SC}(\text{NH}_2)_2]_2^+$  with thiourea, and this has been the basis for a number of schemes proposed for the recovery of gold from ores and concentrates (Groenewald, 1977; Pyper and Hendrix, 1981). Steady-state measurements of the current at a gold electrode at various potentials in an acidic thiourea solution have shown that gold dissolves as gold(I) with a current efficiency of 100% at potentials below about 0.6 V, as shown by the data in Figure 15.5. Comparison of the limiting current with that calculated for the reaction



shows that dissolution is largely diffusion-controlled in the plateau region. The increase in current at higher potentials is accompanied by a decrease in the current efficiency, due to the competitive anodic process of the oxidation of thiourea to formamidine disulphide and, at the highest potentials, to further oxidation products. This irreversible loss of thiourea by oxidation

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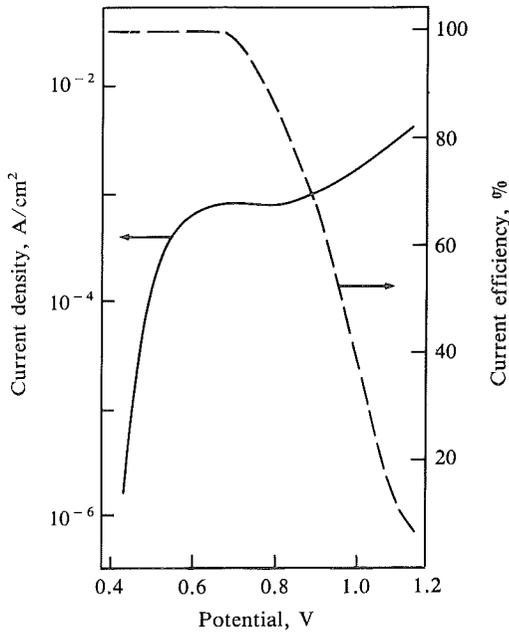


Figure 15.5. Effect of potential on the anodic dissolution of gold and the current efficiency of its dissolution into a solution containing 0,1 M sulphuric acid and 0,1M thiourea at 30°C (after Groenewald, 1977).

is a significant factor in the economic viability of its use in the leaching of gold. The most important point to be learnt from Figure 15.5 is that gold will be leached at a significant rate in thiourea solutions only if the potential can be maintained above 0,4 V, and this requires oxidants such as ferric ions or hydrogen peroxide. The reduction of oxygen is slow at these potentials, and this precludes the use of oxidation by air.

### (c) Cyanide

The electrochemical nature of the dissolution of gold in aerated cyanide solutions is well established, and much work has been published on the anodic behaviour of gold in alkaline cyanide solutions. This subject was recently reviewed (Nicol, 1980b), and therefore only the most important features will be discussed.

Detailed coulometric studies (Kirk *et al.*, 1979) have revealed that the stoichiometry of the anodic dissolution reaction in cyanide solutions is:



throughout the potential range  $-0,65$  to  $0,55$  V. At higher potentials there is evidence of the formation of gold(III) species. A recent review (Nicol, 1980b) demonstrates that the anodic characteristics of gold in cyanide solu-

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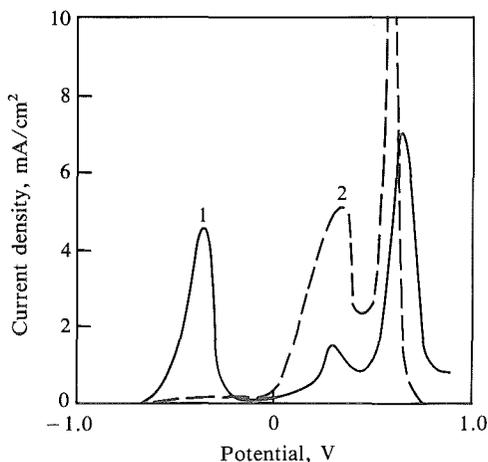


Figure 15.6. Current versus potential curves for the oxidation of gold in alkaline cyanide solutions (after Nicol, 1980b). 1, 0,077 M  $\text{CN}^-$ , pH 12; 2, 0,1 M  $\text{CN}^-$ , 0,1 M  $\text{OH}^-$ .

tions, as reported by different workers, exhibit significant variations. However, examination of the curves (two of which are shown in Figure 15.6) reveals that three peaks occur at potentials of about  $-0,4$  V,  $0,3$  V and  $0,6$  V and are associated with the formation of three passivating films. Those at  $0,3$  and  $0,6$  V are associated with the formation of oxide films, as comparison with the data in Figure 15.3 will show for the peak at  $0,3$  V.

During the cyanidation of gold, the potential does not exceed zero, and therefore it is appropriate to discuss in greater detail the anodic behaviour in the region of the peak at  $-0,4$  V. As was recently pointed out (Nicol, 1980b), the unusually wide scatter in the results obtained by various workers for the activity of gold towards dissolution in this region can probably be traced to the presence of different amounts of heavy-metal impurities in the solutions used. Of these metals, trace amounts of lead, mercury, bismuth and thallium can have profound effects on the anodic characteristics of gold in this region, as shown by the results in Figure 15.7.

On the basis of measurements of the current at various potentials on the active portion of the peak (i.e. at potentials below  $-0,4$  V), and of the variation in current with the concentration of cyanide at constant potential, it is generally accepted that the dissolution of gold occurs by way of the following mechanism:



Passivation is therefore associated with an adsorbed layer of AuCN. An interesting clue to the possible nature of this layer is to be found in the macromolecular structure of solid AuCN, which consists of linear chains in

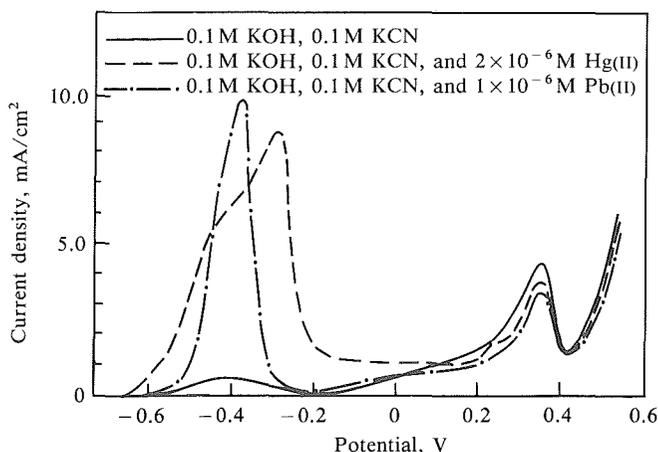


Figure 15.7. Effect of the addition of lead and mercury ions on the anodic behaviour of gold in an alkaline cyanide solution. Before each anodic sweep, the electrode was left under open circuit conditions for 5 minutes (after Nicol, 1980b).

which the cyanide ion functions as a bidentate ligand (Puddephatt, 1978). It is conceivable that this type of structure could develop in two dimensions to form a passive layer. The presence of foreign heavy-metal atoms (such as Pb, Hg or Tl) on the surface would be likely to disrupt the formation of such a layer, thus reducing the extent of passivation.

It should be pointed out that the above observations apply only to the behaviour of pure gold. In actual ores, gold is generally alloyed with other elements such as silver, copper, and in some cases, even mercury. Problems due to passivation of the gold surface under plant leaching conditions could therefore be expected to be minimal. However, much additional research is required to establish the effects of alloying on the anodic behaviour of gold.

#### 15.1.3.2 Anodic reactions of zinc

The precipitation of gold from cyanide solutions by metallic zinc is an electrochemical process in which the zinc dissolves anodically. It is therefore relevant to discuss some of the major aspects of the anodic behaviour of zinc in alkaline cyanide solutions. As pointed out in Section 15.1.2, several zinc species such as  $\text{Zn}(\text{CN})_4^{2-}$  and  $\text{Zn}(\text{OH})_4^{2-}$  can be formed under these conditions, and the electrochemical characteristics of the anodic process are therefore complex, as shown by the current-potential curves shown in Figures 15.8 and 15.9. Therefore, in the absence of cyanide (curve *a* in Figure 15.8), zinc shows little anodic activity at the pH values generally encountered during precipitation. The addition of cyanide results in enhanced currents at potentials above about  $-1.1$  V (curve *b*). In some instances, a plateau is apparent on the curve before the current decreases due to passivation of the surface by a zinc oxide (or hydroxide) species. The plateau occurs because the rate of the reaction

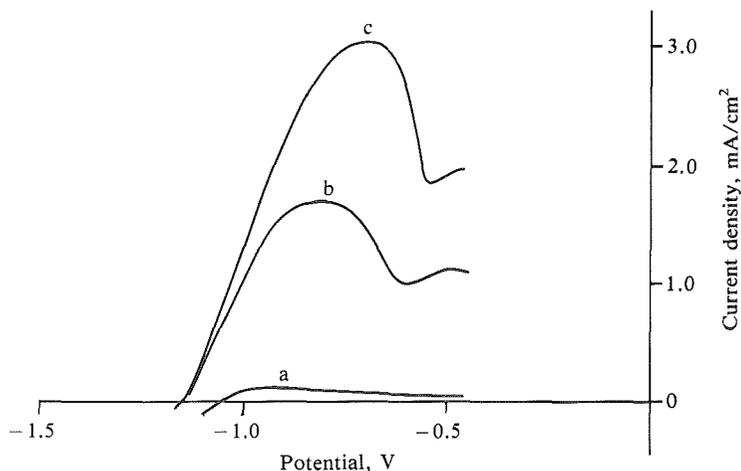


Figure 15.8. Current-potential curves for the anodic dissolution of a rotating zinc-disc electrode in alkaline and alkaline cyanide solutions. (a) 0,005 M  $\text{Ca}(\text{OH})_2$ , 1000 rev/min; (b) 0,005 M  $\text{Ca}(\text{OH})_2$ , 0,005 M NaCN, 250 rev/min; (c) solution as for (b), 1000 rev/min (after Nicol *et al.*, 1979).



becomes controlled by the rate of mass transport of cyanide ions to the surface of the zinc, as shown by the increased height of the plateau at the higher stirring speed (curve c).

As could possibly be expected from the nature of the above reaction, the rate (as measured by the current at a constant potential) increases with increasing cyanide concentration, and this results in both a cathodic shift of the curves and an increased height of the plateau. Furthermore, an increase in the pH of the solution results in similar trends in the curves, due to the formation of soluble zinc hydroxy complexes such as  $\text{Zn}(\text{OH})_4^{2-}$  at pH values above about 12, and to the formation of mixed hydroxycyano complexes at lower pH values. The implications of these characteristics for the efficiency of precipitation of gold will be discussed in detail in Section 15.3.1.

### 15.1.3.3 Cathodic processes

In addition to the obvious and important cathodic reduction of the aurocyanide ion to metallic gold, it is important to review briefly the other cathodic processes that are relevant to the extraction and refining of gold, namely the reduction of oxygen in alkaline solutions and the reduction of the gold chlorides in acidic solutions.

#### (a) Reduction of $\text{Au}(\text{CN})_2^-$

Published information on the reduction of the aurocyanide ion under con-

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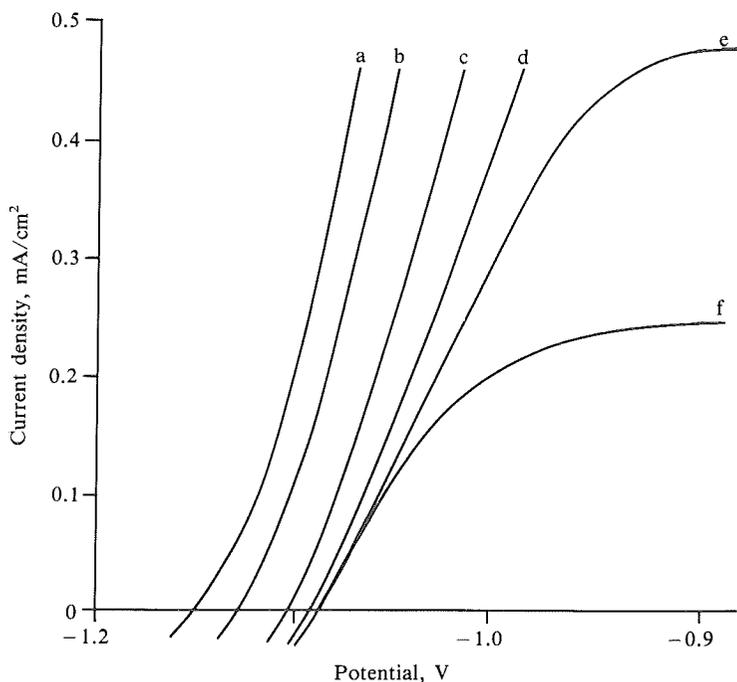


Figure 15.9. Current-potential curves for the anodic dissolution of a rotating zinc-disc electrode in solutions of NaCN and NaCl. *a*,  $2 \times 10^{-2}$  M; *b*,  $10^{-2}$  M; *c*,  $4 \times 10^{-3}$  M; *d*,  $2 \times 10^{-3}$  M; *e* and *f*  $10^{-3}$  M NaCN. All solutions contain  $10^{-2}$  M NaCl at pH 11.0. The speed of rotation of the electrode was 1000 rev/min except for curve *f*, where it was 250 rev/min (after Nicol *et al.*, 1979).

ditions relevant to the processing of gold ores is not extensive, since most workers have concentrated on the somewhat different conditions used in the gold-plating industry. The following will therefore be a summary of work carried out at Mintek (Nicol *et al.*, 1979; Paul *et al.*, 1983) in connection with the cementation and electrowinning of gold.

Figure 15.10 shows current-potential curves for the reduction of  $\text{Au}(\text{CN})_2^-$  at a rotating gold-disc electrode in various deoxygenated solutions. In the absence of  $\text{Au}(\text{CN})_2^-$  (curve *a*), the cathodic current at potentials below  $-1.0$  V is due to the reduction of water to hydrogen and, as has been discussed above, the small anodic current at potentials above about  $-0.4$  V is due to the dissolution of gold. The addition of  $\text{Au}(\text{CN})_2^-$  to the solution results in curve *b*, which displays cathodic currents at potentials below  $-0.5$  V due to the reaction



The rate of reduction increases with decreasing potential until it becomes

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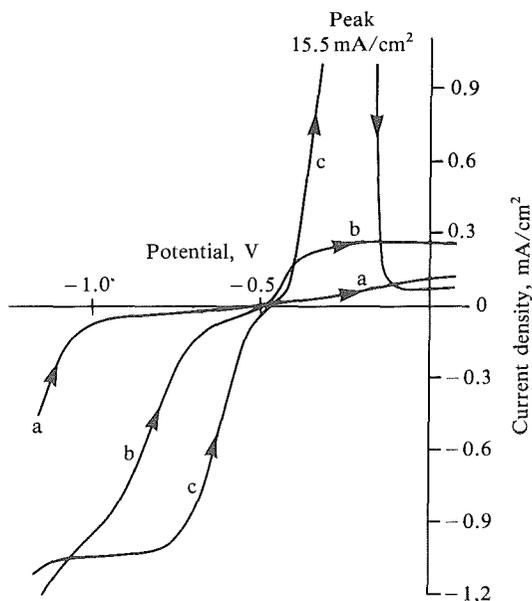


Figure 15.10. Current-potential curves for reactions at a rotating gold-disc electrode ( $r = 1000$  rev/min) in alkaline cyanide ( $0,005$  M NaCN and  $0,005$  M  $\text{Ca}(\text{OH})_2$ ) solutions (*a*, no gold in solution; *b*,  $1,6 \times 10^{-3}$  M gold; *c*  $1,6 \times 10^{-3}$  M gold and  $1,6 \times 10^{-3}$  M lead (after Nicol *et al.*, 1979).

controlled by mass transport of the aurocyanide to the surface at potentials close to  $-1,0$  V. The increased current at more negative potentials is due to the simultaneous evolution of hydrogen. The addition of as little as 3 mg of lead nitrate per litre of solution results in a significant shift of the curve to more positive potentials, i.e. the reduction of aurocyanide is considerably enhanced by the presence of lead in the solution. Similar effects are observed for mercury and thallium, and the catalytic effect of these metal ions on both the anodic and cathodic characteristics of the  $\text{Au}/\text{Au}(\text{CN})_2^-$  couple should be noted.

Variation of pH in the range 10 to 12 has no effect on the curve for the reduction of  $\text{Au}(\text{CN})_2^-$ . However, increasing cyanide concentration results in a shift of the curve to more negative potentials by approximately 0,1 V for each tenfold increase in cyanide concentration. The addition of small amounts of sulphide ions has no noticeable effect on either the anodic or cathodic reaction.

### (b) Reduction of oxygen

The reduction of oxygen by the reaction



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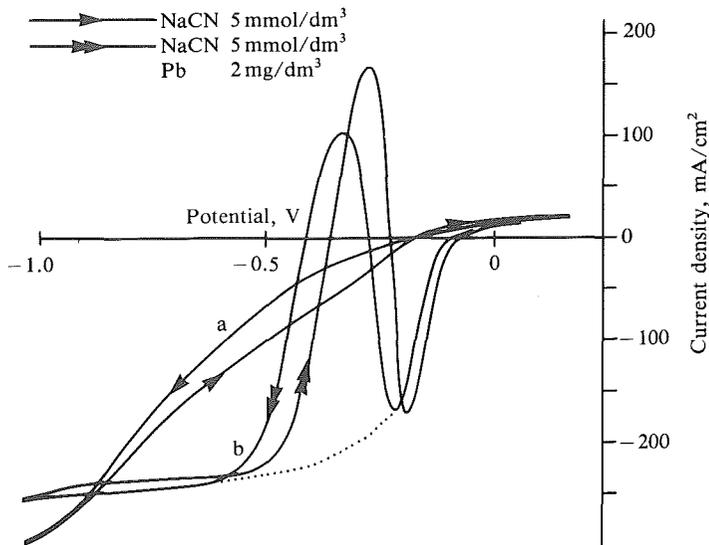


Figure 15.11. Cyclic voltammograms for the reduction of oxygen ( $2,5 \times 10^{-4} \text{ mol l}^{-1}$ ) at a rotating gold disc electrode in solutions of NaCN.

is thermodynamically possible at potentials lower than 0,63 V at pH 10. However, the well-known kinetic inertness of this process, even at precious-metal electrodes, results in large overpotentials for this reaction. In alkaline solutions, therefore, the above reaction proceeds at a significant rate only at negative potentials and, depending on the conditions, becomes mass-transport controlled at potentials below about  $-0,4 \text{ V}$ .

In the absence of cyanide, the reduction of oxygen in alkaline solution has been shown (Damjanovic *et al.*, 1967) to proceed through the intermediate formation of peroxide by the reaction



The extent to which peroxide is further reduced to hydroxide ions is dependent on a number of factors such as pH, agitation, potential, and the presence of trace amounts of heavy-metal impurities in the solutions used.

In the presence of cyanide, the rate of reduction of oxygen is generally slower, as is shown by curve *a* in Figure 15.11. The addition of small amounts of heavy-metal ions such as those of lead, mercury, or thallium results in a considerable enhancement of the rates of anodic dissolution of gold and cathodic reduction of oxygen (curve *b* in Figure 15.11), with the peak for the anodic process now superimposed on that of the cathodic reaction.

### (c) Reduction of $\text{AuCl}_4^-$

As mentioned in Section 15.1.3.1(a), the anodic dissolution of gold results in the formation of gold(I) and gold(III) complexes in various proportions,

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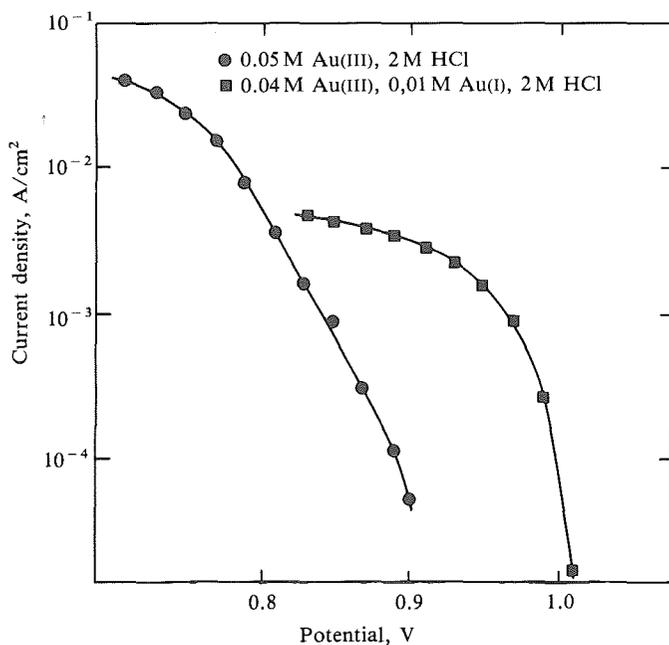
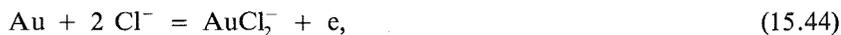


Figure 15.12. Current-potential curves (obtained from the anodic sweeps of cyclic voltammograms) for a rotating (1000 rev/min) gold-plated platinum-disc electrode at 21°C (after Nicol and Schalch, 1976b).

depending on the relative rates of the two consecutive reactions



and



On the other hand, the dissolution of gold by the use of chlorine in concentrated chloride solutions results in the formation of  $\text{AuCl}_4^-$  alone. The reduction of gold(III) chloride to the metal can be expected to involve the formation of gold(I) as an intermediate species, and an extensive investigation (Nicol and Schalch, 1976a) of the cathodic behaviour of gold in chloride solutions has shown that the quality of the cathode deposit is strongly influenced by the relative amounts of gold(I) and gold(III) present in the solution.

An explanation for this observation is to be found in the results in Figure 15.12, which shows that the reduction of  $\text{AuCl}_2^-$  occurs at more positive potentials than that of  $\text{AuCl}_4^-$ . The plateau in the curve for the former at potentials below about 0,65 V occurs because the rate of reduction becomes controlled by the rate of mass transport of  $\text{AuCl}_2^-$  to the surface. Under normal electrorefining or electrowinning conditions, gold will be deposited

from both the gold(III) and gold(I) species. It is well known (Despic and Popov, 1972) that metals deposited at their mass-transport-controlled rates tend to form highly dendritic and powdery deposits. The fact that the cathodes produced during the electrorefining of gold in chloride solutions are generally of poor quality, in that they tend to be bulky and porous, is therefore not unexpected.

The presence of gold fines in the solution as a result of the disproportionation reaction



also creates considerable handling problems in the electrorefining process. From the above it should be apparent that process conditions should be adjusted so as to minimize the amount of gold(I) produced. Detailed studies (Nicol and Schalch, 1976a, 1976b) of the anodic and cathodic reactions have shown that the use of low temperatures and periodic interruption of the current are the major factors that can contribute to reduced gold(I) concentrations.

## 15.2 The Dissolution of Gold

### 15.2.1 The mechanism of cyanidation

The chemistry of the dissolution of gold (and silver) in alkaline cyanide solutions has been the subject of considerable investigation for over a century. Although the overall features of the reactions involved are well established, there is still uncertainty regarding the details of some aspects of the mechanism of the process. Undoubtedly the major advance in the understanding of cyanidation was made by Kudryk and Kellogg (1954), who conducted experiments to demonstrate that the dissolution of gold in cyanide solutions is essentially an electrochemical process.

A simplified schematic diagram, which illustrates the 'mixed-potential' electrochemical model (Figure 15.13), shows that the anodic dissolution of gold in the presence of cyanide ions is coupled to the cathodic reduction of oxygen. Each of these half-reactions has been discussed in detail in previous sections. In the absence of any externally applied current, a gold surface immersed in an aerated alkaline cyanide solution will undergo dissolution at a rate governed by the requirement that the rate of the anodic process is equal to the rate of the cathodic reduction of oxygen. As shown, this will occur at a potential  $E_m$ , known as the mixed potential.

The curves depict the situation generally observed under conditions of 'high-purity'. Data obtained by Kudryk and Kellogg (1954) under conditions that probably resemble more closely those pertaining to plant operation, are shown in Figure 15.14. It is noteworthy that there is no passivation of the anodic reaction, and also that cathodic currents are treated as positive. The plateaus in the anodic curves at potentials above about  $-0,3$  V and low concentrations of cyanide occur because the rate of dissolution becomes limited by the rate of mass transport of cyanide ions to the gold surface. Similarly, the plateau in the cathodic curve at potentials lower than  $-0,5$  V is the

## THE CHEMISTRY OF THE EXTRACTION OF GOLD

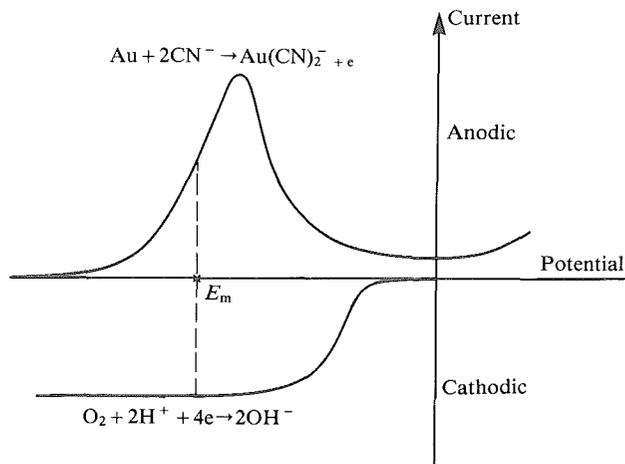


Figure 15.13. Simplified schematic diagram of the mixed-potential model for the dissolution of gold in cyanide solutions.

limiting diffusion current for the reduction of oxygen from dissolved air. Application of the mixed-potential model to these data results in the following predictions.

- i) At low concentrations of potassium cyanide (lower than about 0,017%), the rate of leaching will increase with increasing concentration of cyanide, and the mixed potential will decrease from  $-0,18$  to  $-0,5$  V at 0,005 and 0,017% cyanide respectively.
- ii) At higher concentrations of potassium cyanide, the mixed potential will decrease from  $-0,55$  V to  $-0,75$  V at 0,025 and 0,5% respectively, but the rate of leaching will become independent of the cyanide concentration.
- iii) An increase in the concentration of oxygen by the use of pure oxygen will result in a positive shift of the curve for the reduction of oxygen (shown as the dashed line) with a resulting positive shift in the mixed potential. Under these conditions, it is apparent that, at higher concentrations of potassium cyanide, the rate of dissolution will increase with increasing cyanide concentration, and will become independent of the cyanide concentration only when it exceeds about 0,075%.
- iv) For a given oxygen concentration such as that provided by an air-saturated solution ( $2,5 \times 10^{-4}$  mol l<sup>-1</sup> at 25°C), there will be a particular concentration of cyanide at which the rates of both the anodic and cathodic reactions will be diffusion-controlled. This concentration can be defined as follows.

The maximum rate ( $R_a$ ) of the anodic process



will be given by Fick's first law of diffusion, and can be described by an equation of the form

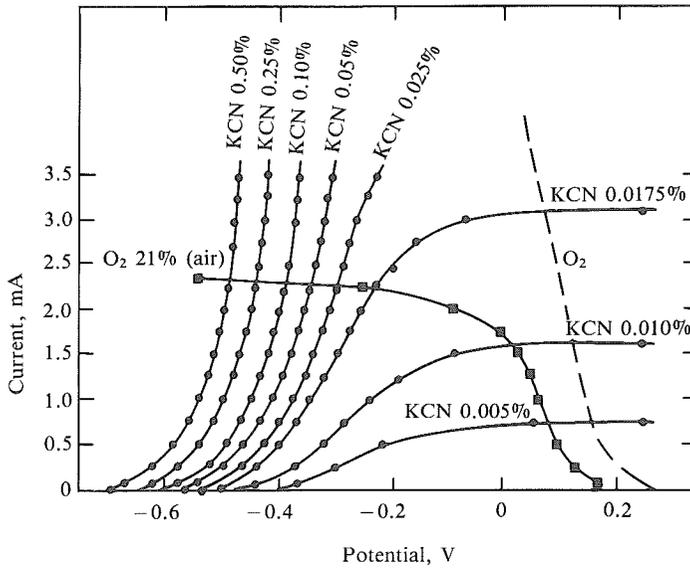


Figure 15.14. Anodic and cathodic current-potential curves for gold (after Kudryk and Kellogg, 1954).

$$R_a = k \cdot D_{CN} \cdot [CN^-] / 2, \tag{15.48}$$

where  $k$  is a constant,  $D_{CN}$  the diffusion coefficient of the cyanide ion, and  $[CN^-]$  the concentration of cyanide. The factor 2 is included because two cyanide ions are required for each electron produced.

Similarly, the maximum rate ( $R$ ) of the cathodic process



will be given by

$$R_c = 4kD_o [O_2], \tag{15.50}$$

where the factor 4 is included because four electrons are accepted by each molecule of oxygen. Equating of these two rates and rearrangement gives

$$[CN^-] = \frac{8D_o}{D_{CN}} \cdot [O_2] \tag{15.51}$$

which, on the substitution of values for the diffusion coefficients and the above concentration of oxygen, yields a potassium cyanide concentration of  $2,5 \times 10^{-3}$  M (or 0,016%). The practical implication of this conclusion is that the rate of leaching in air-saturated solutions will be unaffected by an increase in the cyanide concentration above this level.

Increased rate of cyanidation can be achieved by the use of oxygen instead of air, under pressure if necessary, increased agitation, and elevated

temperatures. These variations are employed in the 'intensive cyanidation' process (Davidson *et al.*, 1978), which is practised on several South African plants for the treatment of gravity concentrates. In this process, concentrates with a gold content as high as 20 kg per ton are subjected to cyanidation under conditions of vigorous agitation with oxygen aeration and cyanide additions as large as 50 kg per ton of concentrate. Under these conditions, over 97% of the gold can be dissolved in 10 to 20 hours. An interesting observation made during the development of this process is that the use of sodium cyanide instead of potassium cyanide results in poorer recoveries from high-grade concentrates, and this was shown to result from partial passivation of the gold surface by the precipitation of the sparingly soluble sodium aurocyanide salt. The use of potassium cyanide obviates this problem because of the greater solubility of the potassium salt.

In practice, it is generally difficult to observe passivation of the gold as described in Section 15.1.3.1(c), and therefore this is not normally considered. However, the literature contains several references to such observations, which indicates that passivation is at least partially responsible for leaching rates that are lower than expected. As a result of testwork with calcine, Cathro (1963) concluded that passivation of the gold surface occurred at high oxygen concentrations in the absence of salts such as those of lead or thallium. In a more extensive study of the leaching and electrochemical behaviour of gold in pyrite concentrates, Filmer (1982) found an inverse relationship between gold extraction and residual sulphur in the calcines. He proposed a mechanism that involves the passivation of gold as a result of the enhanced reduction of oxygen on the pyrite and pyrrhotite surfaces in contact with the gold particles. This galvanic interaction results in a positive shift of the potential of the gold surface, which can result in a mixed potential that is in the passive region, as shown in Figure 15.6. Lead nitrate is generally added to the leaching circuit on a number of plants in an attempt to minimize the deleterious effects of sulphide ions (Section 15.2.2) on the leaching of gold. An additional function of the lead could be to reduce the possibility of passivation by the mechanism outlined in Section 15.1.3.1(c).

### 15.2.2 The effect of other constituents of the pulp

The poor extraction of gold by cyanidation can, in many cases, be attributed to mineralogical factors, such as incomplete liberation of the gold particles (Feather and Koen, 1973), the presence of tarnished or coated gold (Viljoen and Mihalik, 1968), or galvanic contact between gold and pyrite particles, which can result in passivation of the gold surface (Filmer, 1982). The first two of these effects are discussed in other chapters.

Chemical effects that have an adverse influence on either the rate or extent of cyanidation can usually be attributed to one of the following factors:

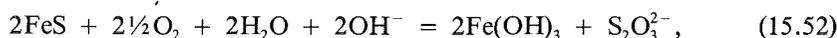
- i) the depletion of cyanide and oxygen in the pulp due to reaction with the constituents of the pulp,
- ii) the adsorption of poisons on the surface of the gold particles, which can retard anodic dissolution of the gold, and

- iii) the presence in the pulp of carbonaceous material which can absorb aurocyanide ions.

The literature contains a large amount of information on the cyanidation of gold, which requires careful analysis if erroneous conclusions are to be avoided. For example, the deleterious effect of nickel on cyanidation reported by Beyers (1936) is probably due rather to the consumption of cyanide that occurs as a result of the formation of the very stable complex  $\text{Ni}(\text{CN})_4^{2-}$  than to any possible effect of the complex itself (Osseo-Asare *et al.*, 1984a). Furthermore, much of the data has been gathered from experiments in which large samples of gold (as leaf, foil, or in polished sections) are contacted with relatively small volumes of cyanide electrolyte for short periods (1 to 2 hours). In such experiments the preparation of the gold surface can influence the rate of cyanidation during the time of measurement, and may not be representative of actual leaching practice.

#### 15.2.2.1 Iron sulphide minerals

The common iron-containing sulphide minerals that are usually associated with gold are pyrite, marcasite, and pyrrhotite. These minerals decompose in aerated alkaline cyanide solutions to various extents, their reactivity increasing in the order pyrite < marcasite < pyrrhotite. In the absence of cyanide ions, the reaction products that have been observed include ferric hydroxide, sulphide, elemental sulphur, thiosulphate, polythionates, and sulphates (Hedley and Tabachnick, 1968). The formation of the higher oxidation states of sulphur consumes both lime and oxygen, e.g.



and

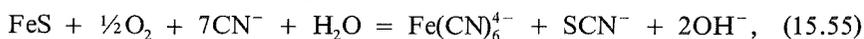


As a result of the high rate of oxidation of pyrrhotite, the dissolved oxygen is rapidly consumed and the concentration of oxygen may become very low. Under these conditions, pyrrhotite may dissolve non-oxidatively, producing sulphide ions and ferrous hydroxide (Gardiner, 1933):



The rates of all these reactions are enhanced by high alkalinities.

In the presence of cyanide ions, both pyrite and pyrrhotite are unstable with respect to oxidation, yielding soluble ferrocyanide and thiocyanate ions as the major products, e.g.:

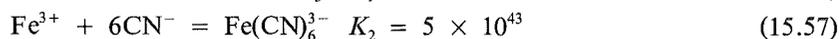
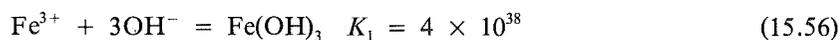


although thiosulphates, polythionates, and sulphates are also produced. It has been reported that ferrocyanide ions inhibit cyanidation (Beyers, 1936; Taylor, 1983), although other workers (Holloway, 1982; Osseo-Asare *et al.*, 1984a) have stated that ferrocyanide has no effect on cyanidation. The latter view is probably correct, but the consumption of oxygen and cyanide required for the formation of ferrocyanide could appreciably affect the cyanidation of gold.

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Although ferrocyanide ions are thermodynamically unstable with respect to their oxidation to ferricyanide ions ( $E^\circ = 0,46$  V) by dissolved oxygen ( $E = 0,58$  V at a pH of 11), the rate of oxidation is very low (Hedley and Tabachnick, 1968). Strong oxidants such as permanganate ions and ozone oxidize ferrocyanide very rapidly, and the resulting ferricyanide can oxidize gold in the presence of cyanide ions (Putnam, 1950).

There is no general agreement as to the best procedure to be used in the cyanidation of ores containing iron sulphide minerals. In many cases, the addition of sufficient quantities of air and cyanide may be all that is required for adequate dissolution of the gold. If the consumption of cyanide is excessively high, aeration in alkaline solution prior to the addition of cyanide may be required (Gardiner, 1933; McLachlan *et al.*, 1946). The aim of this treatment is partial oxidation of the surface of the sulphide particles and the production of a surface film of ferric hydroxide that will inhibit further leaching of the sulphides upon the addition of cyanide ions. It is important to note that ferric hydroxide is practically insoluble under the conditions of cyanidation, since the concentration of soluble ferricyanide in equilibrium with ferric hydroxide at a pH of 11 and a free cyanide concentration of  $10^{-3}$  mol l<sup>-1</sup> is  $1,3 \times 10^{-4}$  mol l<sup>-1</sup>:



$$[\text{Fe}(\text{CN})_6^{3-}] = \frac{K_2 [\text{CN}]^6}{K_1 [\text{OH}]^3}.$$

As a result, the consumption of cyanide is greatly reduced. During pre-aeration, the pH value should be maintained below 12 so that the formation of excessive amounts of sulphide ions, which have a deleterious effect upon cyanidation, can be avoided (see below).

### 15.2.2.2 Copper sulphide minerals

The most common copper sulphide minerals associated with gold are chalcopyrite and chalcocite. In a typical cyanide electrolyte, chalcocite is somewhat more reactive than chalcopyrite, although both are oxidized to soluble copper cyanide complexes and thiocyanate (McLachlan *et al.*, 1946). These minerals may therefore retard the cyanidation of gold, due to their consumption of oxygen and cyanide ions.

The only stable oxidation state of copper in the presence of cyanide ions is +1, since any cupric ions are reduced to cuprous ions by the oxidation of cyanide ions to cyanogen. An increase in the concentration of cyanide ions results in the formation of the complexes



$\text{Cu}(\text{CN})_3^{2-}$  being the predominant species under the conditions of cyanidation (Osseo-Asare *et al.*, 1984a; Shantz and Reich, 1978).

Hedley and Kentro (1945) investigated the effect of soluble copper in cyanide solutions on the dissolution of gold from ores and pure gold. The

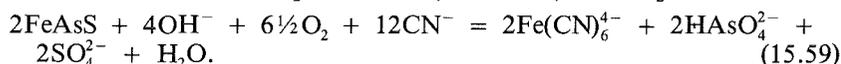
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rate of dissolution in an electrolyte containing cyanide and copper at a molar ratio of 3 to 1 was about 60% of the value obtained with an electrolyte with a pure sodium cyanide content of 0,01 to 0,05%. At a molar ratio of 4 to 1, the rate of dissolution approached that obtained with the pure electrolyte. Similar results have been reported by McLachlan *et al.* (1946).

The conclusion to be drawn from these results is that the cupro-cyanide complexes have no effect upon the cyanidation of gold provided that sufficient excess free cyanide is available. Stamboliadis *et al.* (1976) concluded that the presence of soluble cupro-cyanide complexes retards the dissolution of gold, even when sufficient lime, cyanide, and oxygen are present. However, the titration method they used to determine the concentration of free cyanide ions may have yielded erroneously high values (Shantz and Reich, 1978).

### 15.2.2.3 Arsenic sulphide minerals

The common arsenic sulphide minerals associated with gold are arsenopyrite ( $\text{FeS}_2 \cdot \text{FeAs}_2$  or  $\text{FeAsS}$ ), realgar ( $\text{AsS}$ ), and orpiment ( $\text{As}_2\text{S}_3$ ). These minerals are all decomposed in oxygenated alkaline solutions, the reactivity increasing in the order  $\text{FeAsS} < \text{AsS} < \text{As}_2\text{S}_3$  (Hedley and Tabachnick, 1968). The stable oxidation products are  $\text{HAsO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Fe}(\text{CN})_6^{4-}$  (in the case of arsenopyrite), e.g.



These reactions consume large quantities of oxygen, lime ( $\text{AsS}$  and  $\text{As}_2\text{S}_3$ ), and cyanide ( $\text{FeAsS}$ ), and may therefore retard the cyanidation of gold to a large extent. During the cyanidation of ores containing these minerals, many other compounds, in addition to those mentioned above, are produced, e.g.  $\text{S}^{2-}$ ,  $\text{SCN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{AsS}_3^{3-}$  and  $\text{HAsO}_3^{2-}$  (Nagy *et al.*, 1966). If an adequate supply of oxygen is available, however, the intermediate products such as thioarsenite,  $\text{AsS}_3^{3-}$ , and arsenite,  $\text{HAsO}_3^{2-}$ , will be oxidized to arsenate ions.

Apart from the consumption of oxygen, there appears to be no evidence to indicate that any of the arsenic-oxygen compounds has any chemical effect on the cyanidation of gold. Hedley and Tabachnik (1968) have suggested that the adsorption of thioarsenite ions onto the surface of the gold particles may retard dissolution. The deleterious effect of sulphide ions on cyanidation is generally acknowledged (see below). The addition of lead nitrate has been shown to enhance the oxidation of both sulphide and thioarsenite ions.

### 15.2.2.4 Antimony sulphide minerals

The only antimony sulphide mineral associated with gold is stibnite,  $\text{Sb}_2\text{S}_3$ , the chemistry of which is very similar to that of  $\text{As}_2\text{S}_3$ . In alkaline solutions stibnite is oxidized to antimonites ( $\text{HSbO}_3^{2-}$ ), antimonates ( $\text{HSbO}_4^{2-}$ ), and thioantimonites ( $\text{SbS}_3^{3-}$ ), which consume lime and oxygen. The rate of oxidation of stibnite, like that of arsenic minerals, is enhanced by a high

pH value (i.e. above 12), (Muir *et al.*, 1984).

Hedley and Tabachnick (1968) have suggested that thioantimonites can retard the dissolution of gold by being adsorbed onto the surface of gold particles. Aeration in alkaline electrolytes (pH 10 or lower) prior to the addition of cyanide ions can result in improved dissolution of gold. Lead nitrate can be added to accelerate the oxidation of sulphide and thioantimonite ions.

If the antimonial ore is roasted for the removal of volatile antimony oxides, the temperature and air flow must be carefully controlled if the production of metallic antimony, which can coat the surface of the gold particles, is to be avoided (Nagy *et al.*, 1966). Ores containing silver may form 'antimony glasses' ( $x\text{Ag}_2\text{O}\cdot y\text{Sb}_2\text{S}_3$ ) during roasting (Matsukawa and Sakai, 1956).

#### 15.2.2.5 Anions containing sulphur

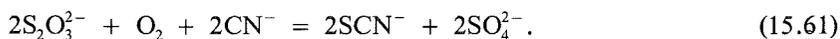
The sulphur anions that are known to be strong 'poisons' in the cyanidation of gold are sulphide, thioarsenite, and thioantimonite ions. Fink and Putnam (1950) showed that concentrations of dissolved sulphide as low as  $0,5 \text{ mg l}^{-1}$  can halve the rate of leaching, and attributed this retardation to the formation of insoluble aurous sulphide on the surface of the gold particles. Hedley and Tabachnick (1968) suggested that sulphide, thioarsenite, and thioantimonite ions could be strongly adsorbed onto gold surfaces, thus rendering the surfaces inert towards cyanide and oxygen.

Although these sulphur anions are thermodynamically unstable towards oxidation by dissolved oxygen in alkaline solutions, the rate of oxidation can be remarkably low. The addition of lead (as the nitrate, acetate, or litharge) can enhance the rate of oxidation markedly. In the case of sulphide ions, this effect has been attributed to the presence of precipitated lead sulphide, which presents a large surface area for the reduction of oxygen and the oxidation of the residual sulphide (Paul, 1984).

Thiosulphate and polythionate ions are produced during the oxidation of many sulphide minerals, and are unstable towards further oxidation if dissolved oxygen is present, e.g.



They also react slowly with cyanide in the presence of dissolved oxygen, forming thiocyanate:



Although these compounds can consume lime, oxygen, and cyanide ions, they do not appear to exert any direct influence on the dissolution of gold.

Thiocyanate ions can be produced in relatively large amounts by the oxidation of some sulphide minerals. These ions do not appear to have any effect on the cyanidation process.

#### 15.2.2.6 Cyanide complexes of various base metals

The presence of the cyanide complexes of  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  have no direct effect upon cyanidation, although the formation of these com-

plexes may deplete the leach liquor of free cyanide, and retard the dissolution of gold. Ferricyanide is an oxidant that can actually leach gold (Putnam, 1950).

Low concentrations of  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Bi^{3+}$  and  $Tl^{+}$  can enhance the leaching of gold under certain conditions (Fink and Putnam, 1950; Cathro, 1963). The electrochemical aspects of this effect have been discussed by Nicol (1980a). It is generally agreed that the anodic dissolution of gold in cyanide solution is a multistep reaction that involves the reactions



If the rate of the electrochemical production of the adsorbed  $AuCN_{ads}$  is higher than the rate at which the adsorbed species is removed as  $Au(CN)_2^{-}$ , a macromolecular layer of  $AuCN$  may be formed on the surface of the gold. The presence of small amounts of the heavy-metal ions cited above may inhibit the formation of this passivating layer, thereby enhancing the rate of the overall reaction.

#### 15.2.2.7 Calcium ions

Calcium ions are introduced into the cyanide pulp in the form of lime, which is the most commonly used protective alkali, and as calcium cyanide. Barsky *et al.* (1935) reported that the rate of cyanidation decreased when the pH value was raised above 11 with lime, and that almost no leaching of gold occurred at a pH of 12.2. However, if the pH value was adjusted with sodium hydroxide, the rate of cyanidation was unaffected for pH values up to 12.5. On the other hand, the addition of calcium chloride to an alkaline cyanide solution had no effect on the dissolution of gold.

It was concluded that high concentrations of both calcium and hydroxide ions must be present for the effect to be observed. The reason for this effect is not clear. It has been suggested that the retardation is due to the precipitation of calcium peroxide at the gold surface (Kameda, 1949), but this is most unlikely.

#### 15.2.2.8 Carbonaceous material

The deleterious effects of carbonaceous material or 'preg-robbing' constituents in the pulp, is well known, and only some pertinent review papers are cited (Osseo-Asare *et al.*, 1984b; Nagy *et al.*, 1966; and Eisele *et al.*, 1983). Carbonaceous material can reduce the recovery of gold by restricting the release of gold from the carbonaceous matrix, or by adsorbing dissolved gold from the leach liquor (Osseo-Asare *et al.*, 1984b). The treatment of these ores involves roasting, addition of kerosene or heavy oils, flotation, and aqueous chlorination.

Carbonaceous matter appears to consist of heavy hydrocarbons, which do not interact with gold, an elemental carbon component, which behaves like activated carbon and therefore adsorbs gold, and organic acids (notably humic acids), which can form complexes with dissolved gold (Osseo-Asare *et al.*, 1984b).

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The functional groups on the surface of the elemental carbon component consist of carboxylic ( $R-COOH$ ), phenolic-hydroxyl ( $R-OH$ ), and quinone-type carbonyl ( $R-C=O$ ) groups ( $R$  being an aliphatic or cyclic compound). In alkaline solutions, these groups exhibit a slight negative charge, and it is not clear how interaction with the negatively charged aurocyanide ion occurs. The adsorption of gold is enhanced by the presence of calcium ions, and may therefore require the formation of ion pairs, as has been suggested for the adsorption of gold by activated carbon (Davidson, 1974).

Humic acids also contain functional groups of the type found in the elemental carbon component, and exhibit similar behaviour. The mechanism of the interaction between aurocyanide ions and humic acids remains unresolved.

### 15.2.2.9 Flotation reagents and other surface active reagents

Gold bearing ores are often subjected to flotation before cyanidation. When the flotation concentrate is cyanided without prior calcining, the dissolution of gold is often found to be poor. Whether this phenomenon is due to the 'lock-up' of finely divided gold in the sulphide minerals, the consumption of oxygen or cyanide by the corroding minerals, the presence of sulphide ions in the leach liquor, the presence of residual flotation reagents, or any combination of the above factors, is difficult to elucidate. It is not surprising, therefore, that relatively little has been published on this subject.

In a review of this subject, Finkelstein (1972) concluded that thiol-type collectors (xanthates, dithiophosphates, etc.) can be strongly adsorbed onto gold, thus rendering the surfaces passive and retarding the anodic dissolution process.

### 15.2.3 Other leaching processes

In recent years, increasing emphasis has been placed on protection of the environment from pollution, on the treatment of refractory gold ores, and on underground processing. This has led to renewed interest in the development of leaching processes that are as efficient and as cost-effective as cyanidation, but more environmentally acceptable and less susceptible to the deleterious effects of some constituents of refractory ores.

The thermodynamic behaviour of some of the more important gold complexes is summarized in Figure 15.15, which compares the standard reduction potentials of the gold(III)-gold and gold(I)-gold couples (Nicol, 1980b). The points below the diagonal line correspond to ligands,  $L_1^-$  that form complexes with gold(III),  $AuL_2^{2-}$  which are more stable than the corresponding gold(I) complexes,  $AuL_2^-$ . The latter are the preferred species for those ligands above the line. The standard potentials for the ferric-ferrous couple in acid solution and the oxygen-water couple in acidic and basic solutions are also shown.

The more important of these potential lixivants, excluding cyanide, will be discussed in relation to this figure.

**15.2.3.4 Chloride**

Chlorination was widely used for the leaching of ores during the second half of the nineteenth century. With the advent of the cyanide process, and the steadily decreasing grade of the ores being treated, this method has essentially disappeared, and is at present employed only in the refining of gold. As can be seen from the data in Figure 15.15, the oxidation of gold in chloride solutions occurs at potentials above 1,2 V, and this requires strong oxidants such as chlorine or ozone, the former generally being employed. The use of acidic solutions during chlorination overcomes any passivation problems, since the mixed potential is below that at which oxide films form on a gold surface under these conditions (see Figure 15.4). As shown in Section 15.1.3.1(a), the oxidation of gold in chloride solutions proceeds through the intermediate formation of gold(I) and, in the presence of excess chlorine, gold(III) is the final product:



The rate of dissolution of gold by chlorination is about two orders of magnitude greater than that in cyanidation mainly because the solubility of chlorine is greater than that of oxygen in aqueous solutions.

Under the strong oxidizing conditions employed during chlorination, the dissolution of other metals in the ore is appreciable, even sulphur, in the form of sulphide minerals, being oxidized to sulphate. The excessively high consumption of chlorine by these unwanted reactions renders chlorination uneconomical except under exceptional circumstances such as the recovery of gold from antimonial slags (Muir *et al.*, 1983). An additional disadvantage is that silver chloride is only partially soluble in concentrated chloride solutions, and therefore reports to both the leach residue and the pregnant solution.

**15.3 The Recovery of Gold from Solution**

**15.3.1 Cementation**

The zinc-cementation process for the recovery of gold and silver from cyanide solutions was introduced in 1890. During the following thirty years, three major modifications were introduced that improved the efficiency of the process. These innovations involved the addition of lead salts to the pregnant solution (1894), the use of zinc dust in place of zinc shavings (1897), and de-aeration of the pregnant solution prior to cementation (1916). The historical review compiled by Leblanc (1942) on the recovery of gold from pregnant liquors gives an excellent account of these early developments.

Once the major metallurgical and economic shortcomings of the process had been resolved, the incentive for further research in this area largely fell away. Fortunately, the rekindled interest in electrochemistry which began in the 1960's led to research into the mechanism of cementation, and much of the mystique has been stripped away.

The thermodynamic and kinetic aspects of the cementation process have

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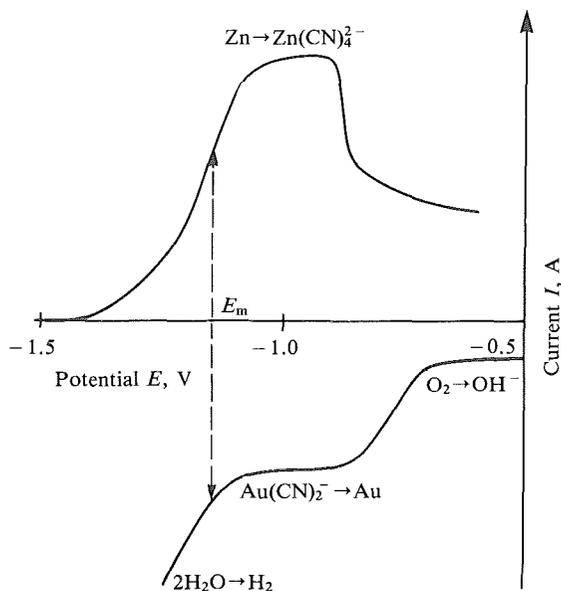


Figure 15.16. Current-potential curves for the major reactions which occur during the cementation of gold onto zinc.

already been introduced. The major reactions are the cathodic deposition of gold onto the surface of the corroding zinc particles:



Other reactions that can influence the cementation process are the reduction of water and dissolved oxygen:



and



The flow of electrons (i.e. electrical current) required to sustain the three cathodic reactions (15.66), (15.68) and (15.69) is supplied by the oxidation of the zinc. The current-potential curves corresponding to these reactions are shown in Figure 15.16.

The potential at the surface of the zinc particles (the mixed potential,  $E_m$ ) is uniquely determined by the currents of all four reactions. Cementation usually occurs with a mixed potential between  $-1.0$  and  $-1.2$  V (Nicol *et al.*, 1979). Over this range, the rates of reactions (15.66) and (15.69) are controlled by the transport of cyanide ions and oxygen to the surface of the zinc particles (Kakovskiy and Shcherbakov, 1967), whereas reactions (15.67) and (15.68) are under activation control.

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An increase in the concentration of cyanide ions causes the curves for both the dissolution of zinc and the deposition of gold (and thus,  $E_m$ ) to shift in a negative direction by 0,12 V for every tenfold increase in the cyanide concentration. This shift increases the evolution of hydrogen (Equation 15.68), thus increasing the consumption of zinc. Furthermore, the generation of gas bubbles can disrupt the flow of solution through the zinc bed and reduce the overall efficiency of the process (Paul, 1985). A decrease in the concentration of free cyanide causes the potential to shift in a positive direction, and may cause the dissolution of zinc to become controlled by the transport of cyanide ions to the zinc surface. Under these conditions, the concentration of cyanide ions at the zinc surface may be so low that zinc hydroxide is precipitated, which prevents any further dissolution of the zinc. The deleterious effects of excessive and insufficient concentrations of free cyanide were reported by Leblanc (1942), who recommended that the concentration of free cyanide should be maintained at between 0,006 and 0,015% sodium cyanide.

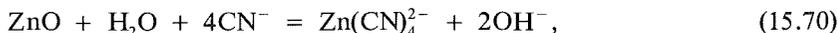
The pH of the pregnant solution in a conventional gold plant usually lies in the range 10,5 to 11,0. Nicol *et al.* (1979) have shown that the current-potential curve for the anodic dissolution of zinc is shifted in a negative direction with rising pH. In addition, at pH values above about 11, the mass-transport peak is increased, owing to the formation of soluble zincates and mixed hydroxy-cyanide complexes. The resulting negative shift in  $E_m$  can be beneficial if the deposition of the gold was not entirely under mass-transport control. Leblanc (1942) reported that the cementation of gold was practically constant over the pH range 8 to 11, but that a marked improvement could be obtained by an increase in pH to a value between 11,5 and 11,9. At very high pH values (i.e. above 13), which may be encountered in carbon-in-pulp (CIP) eluates, the negative shift in  $E_m$  results in the evolution of excessive hydrogen, which has a deleterious effect on cementation. Plaskin *et al.* (1948) reported that the recovery of gold was maximized at a sodium hydroxide concentration of 0,025% (a theoretical pH value of 11,8).

Concentrations of  $Pb^{2+}$  as low as 1 to 2 mg l<sup>-1</sup> have been shown to shift the current-potential curve for the deposition of gold in a positive direction by as much as 0,20 V (Nicol *et al.*, 1979; Kirk and Foulkes, 1984; McIntyre and Peck, 1976). The mechanism associated with this considerable enhancement is not clear. Similar effects have been found with thallium; mercury and bismuth ions (McIntyre and Peck, 1976). Other benefits arising from the addition of lead include reduced zinc consumption (Leblanc, 1942), probably due to an increased overpotential for the evolution of hydrogen, and the precipitation of any sulphide ions as PbS (see below). The addition of lead to above 10 mg l<sup>-1</sup> may actually retard the cementation of gold (Nicol *et al.*, 1979; Leblanc, 1942), as the result of a combination of factors: the effect of the lead on the dissolution of the zinc and the difficulty with which gold nucleates on a lead surface.

Inefficient de-aeration of the pregnant solution accelerates the corrosion of zinc. If insufficient free cyanide is present in the solution, zinc hydroxide will be produced, which results in passivation of the zinc surface. Even

if passivation does not occur, a positive shift in  $E_m$  due to the additional cathodic current may adversely affect the deposition of gold.

The zinc metal used for cementation must clearly have a large surface area, because the overall rate of any electrochemical solid-liquid reaction is directly proportional to surface area. Zinc dust fulfils this requirement, but is readily oxidized by atmospheric oxygen during storage. The coating of zinc oxide must be dissolved before cementation can occur,

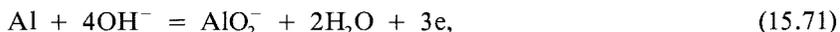


which accounts for the frequent necessity for circulation of the pregnant solution for considerable lengths of time at the start-up of a Merrill or Stellar filter. High concentrations of free cyanide may be beneficial during this period.

The most common impurities including sulphite, sulphate, thiosulphate, ferrocyanide, zinc cyanide, thiocyanate, copper, nickel and cobalt, appear to have little or no effect on the cementation process (Nicol *et al.*, 1979; Leblanc, 1942), although deleterious effects can be observed if the concentrations are very high. Plaskin *et al.* (1948) reported that copper adversely affected the cementation of gold, which almost ceased at a copper concentration of  $200 \text{ mg l}^{-1}$ . However, the deleterious effect of copper decreases as the concentration of cyanide is increased, from which it can be inferred that the effect of copper may be due to a reduction in the concentration of free cyanide as a result of the formation of cyanide complexes. Hancock and Thomas (1954) reported that nickel at concentrations higher than  $200 \text{ mg l}^{-1}$  has a slightly retarding effect on cementation.

The only species that have a marked deleterious effect on cementation appear to be sulphide ions and soluble compounds of arsenic and antimony (Nicol *et al.*, 1979; Leblanc, 1942; Plaskin *et al.*, 1948). The effects are observed even at very low concentrations ( $1 \text{ mg l}^{-1}$  and lower). The poisoning effect of sulphide ions is thought to be due to the precipitation of insoluble zinc sulphide on the surface of the zinc particles. No satisfactory mechanism has been proposed for the effect of arsenic and antimony.

Aluminium is sufficiently electronegative to reduce aurocyanide ions to gold, and its use as a cementing agent was patented by Moldenhauer in 1893. The factor mitigating against its use is the dissolution reaction



which requires the pH value of the solution to be above 12 in order that  $\text{Al}^{3+}$  can be maintained in a soluble form. Furthermore, calcium aluminate has a low solubility, and the use of sodium hydroxide or sodium carbonate is required to adjust the pH; the use of lime must be avoided. A historical review of the use of aluminium for the cementation of gold has been compiled by Nagy *et al.* (1966).

### 15.3.2 Extraction by activated carbon, ion-exchange resins or organic solvents

These three processes have very similar broad metallurgical objectives. In

each case, an aqueous solution containing a mixture of ions is contacted countercurrently with an immiscible extractant phase. The extractant phase either contains chemical functional groups or a heterogeneous surface, which enable the desired metal ion to be extracted (selectively, if possible) from the aqueous phase into the extractant phase. The reactions are reversible so that, after separation of the extractant from the aqueous phase, the desired metal ion can be subsequently stripped into another aqueous phase. The stripping step should result in the production of a purified and more concentrated aqueous metal-ion solution, and should allow the extractant to be recycled to the aqueous feed solution.

In ion exchange, the extractant is a solid organic polymer; in solvent extraction, it is a water-immiscible organic liquid; and in activated carbon the raw material is granular coconut shell, fruit pits, coal, peat, lignite, or wood, which is first charred at 300 to 400°C and then activated (usually in an atmosphere of steam) at 800 to 950°C. In principle, all three techniques could compete favourably with the traditional zinc cementation route for the recovery of gold from cyanide solutions. It is possible, in theory at least, to achieve greater selectivity than can be achieved with zinc, and it is also practical, in each case, to recycle the extractant after the gold has been recovered, because the extractant generally does not undergo chemical change during a loading-stripping cycle. This is not the case with the zinc route. Another major advantage is that, in principle, each of the three techniques can be applied directly to pulps — the carbon-in-pulp (CIP), resin-in-pulp (RIP), and solvent-in-pulp (SIP) processes — which enables the costly filtration and clarification stages to be dispensed with, and the attendant losses of soluble values in the filter cake to be avoided. As discussed elsewhere in this chapter, the CIP process has been introduced in all the major gold-producing countries of the world and is now the preferred route for the recovery of gold in all new gold plants in the western world. The RIP process has been designated the preferred technique for use on new plants in the Soviet Union (Guchetl and Lezgintsev, 1968), and is currently attracting interest in the West. The major problem with SIP is the loss of organic solvent due to its entrainment in the pulp, but a promising development is the SIP contactor in which these losses are minimized (Byerlee, 1980). At the time of writing, however, SIP is regarded rather as an engineering curiosity than a serious competitor with the zinc-cementation, CIP, or RIP processes.

The chemistry of these processes is complex and can be treated here only in the barest outline. For further details, the reader is referred to works devoted specifically to these subjects (Helferrich, 1962; Marcus and Kertes, 1969).

### *15.3.2.1 The activated-carbon process*

#### *(a) The adsorption of gold from cyanide solution*

The use of activated carbon in the recovery of gold has undergone a major revolution in the past ten years. In particular, the CIP process, which involves the use of granular activated carbon for the extraction of dissolved gold directly from pulps or slimes, has been shown to offer significant cost

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advantages over the conventional gold-recovery process in most applications, and the CIP process is now used in all the major gold producing countries.

With CIP technology, as with most new technologies, a fundamental understanding of the mechanisms involved in the adsorption and elution of aurocyanide onto carbon has lagged somewhat behind the engineering and implementation of the process. For all the first-generation CIP plants, therefore, it was necessary to adopt empirical or semi-empirical approaches in the selection of activated carbon products and the derivation of optimum operating conditions. In the last few years, however, a number of publications dealing with the fundamental aspects of the process have appeared and, although the various research groups active in the field have not reached consensus, a coherent picture is beginning to emerge.

Most of the studies have focused on the interaction between the aurocyanide ion and activated carbon, and a number of thermodynamic and kinetic characteristics of the reaction have been identified. Some of these characteristics contradict one another when viewed from the perspective of, for example, the simple electrostatic interaction between metal anions and anion-exchange resins, and no mechanism that adequately accommodates all the observations has been developed. The reaction appears to be fairly unique, and efforts to develop a mechanism in terms of other well-known heterogeneous processes have failed.

A number of experimental observations relating to the aurocyanide-carbon interaction have been drawn from Davidson (1974), Davidson and Duncanson (1977), Dixon *et al.* (1978), McDougall *et al.* (1980), Fleming and Nicol (1984), and Tsuchida *et al.* (1984), and are summarized below.

*Kinetic characteristics.* During thermal activation, carbon develops a porous graphitic structure of molecular dimensions, which creates an enormous internal surface area of the order of 800 to 1200 m<sup>2</sup>g<sup>-1</sup>. The internal pores are classified as macropores (500 to 200 000 Å), mesopores (100 to 500 Å), and micropores (8 to 100 Å). Evidence suggests that at least 90% of the total surface area of the activated carbons used in gold processing is in the micropore category, and that this surface is either inaccessible to the fairly large aurocyanide molecule, or is accessible only after extremely slow diffusion. This property of activated carbon accounts for many of the observed kinetic phenomena in the processing of gold cyanide.

Plant experience and numerous laboratory investigations have shown that the initial rate of adsorption of aurocyanide onto carbon is rapid, and is controlled by the hydrodynamics in the adsorption contactor. This initial film-diffusion-controlled reaction, which presumably involves adsorption in the macropores and mesopores, results in the establishment of a pseudo-equilibrium in 4 to 48 hours\*. Subsequently, gold cyanide continues to be

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\*The exact time taken for the adsorption reaction to reach this pseudo-equilibrium is governed by factors such as pulp density and viscosity, mixing efficiency, carbon particle-size and pore-size distribution, and the presence in the pulp of species that adsorb onto and poison carbon.

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adsorbed onto the carbon almost indefinitely and, in practice, it is difficult to establish a true equilibrium. During this period of pore-diffusion-controlled adsorption, gold cyanide presumably diffuses slowly into the micropores of the carbon and, as the cross-sectional area of the micropores approaches that of the aurocyanide ion, the resistance to mass transfer becomes infinite. Obviously, gold that diffuses very slowly into the micropores will diffuse out only very slowly, and it is probably this fact that has led to confusion regarding the reversibility of the reaction.

From a practical point of view, therefore, the interaction between aurocyanide and carbon can be considered to possess two thermodynamic regimes, the macropore-mesopore equilibrium and the total equilibrium, and the value of the former could be smaller than the value of the latter by a factor of at least 10. What is most significant from a practical point of view, however, is that the pseudo-equilibrium apparently responds to its chemical environment, and is influenced by the thermodynamics of the adsorption reaction in much the same way as a true equilibrium would be. It is not a well-defined entity, however, due to the unhomogeneity of the pore-size distribution from one carbon particle to another and from one batch of carbon to another. Therefore, since the pseudo-equilibrium is not well-defined theoretically, and the true equilibrium is not readily determined experimentally, it is difficult to model the aurocyanide-carbon interaction accurately on the basis of the intrinsic thermodynamic properties of the system. Hence, empirical or semi-empirical approaches based on the rate of adsorption are generally adopted when modelling this reaction. (Hussey *et al.*, 1978; Cho and Pitt, 1979; Nicol *et al.*, 1984a and 1984b; Van Deventer, 1984; and Williams and Glasser, 1985.)

It is apparent that the plant-operating parameters should be set in such a way that the carbon loading is maintained within the macropore-mesopore equilibrium range. The rate of extraction is fast and responsive to good mixing efficiency in the adsorption contractors, and the rate of elution and the ultimate efficiency of elution, under a given set of conditions, are also maximized. Most plants do, in fact, operate predominantly in the pseudo-equilibrium range, with average carbon residence times of about 24 hours per contractor, but there is an obvious economic trade-off between carbon loading and operating costs in elution and reactivation (Nicol *et al.*, 1984b).

*Thermodynamic characteristics.* The chemical nature of the surface of activated carbon has not been firmly established, mainly because of the lack of a suitable physical technique for the direct study of carbon surfaces. Activated carbons have traditionally been divided into two types, those formed at 700 to 1000°C, which extract acid from water, and those formed at 300 to 400°C, which take up base. Carbons used for gold adsorption are usually activated between 700 and 800°C, and show both acid- and base-extracting properties. These properties are consistent with the presence of carboxylic acid and phenolic groups on the surface and, possibly, in addition to these, quinone, chromene, and peroxide groups.

The gold-loading capacity of activated carbon increases with increasing concentration of cations in solution in the order  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{H}^+ >$

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$\text{Li}^+ > \text{Na}^+ > \text{K}^+$ , but decreases with increasing concentration of anions in solution in the order  $\text{CN}^- > \text{S}^{2-} > \text{SCN}^- > \text{SO}_3^{2-} > \text{OH}^- > \text{Cl}^- > \text{NO}_3^-$ . A salt such as  $\text{CaCl}_2$  therefore enhances loading, whereas potassium cyanide inhibits it.

In the presence of aurocyanide or silver cyanide, cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  are co-extracted by activated carbon, but they are not loaded in the absence of the metal cyanide complexes. However, the concentration of cations on the carbon is generally too low to accommodate a simple ion-pair adsorption mechanism.

The adsorption of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  increases with increasing pH, whereas the adsorption of aurocyanide decreases. For  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , this is associated, to a certain extent, with precipitation of the carbonate compounds within the carbon matrix.

A neutral complex such as  $\text{Hg}(\text{CN})_2$  is adsorbed onto activated carbon as strongly as anionic complexes such as  $\text{Au}(\text{CN})_2^-$  and  $\text{Ag}(\text{CN})_2^-$ , but the adsorption of neutral compounds is not influenced by the ionic strength of the solution.

The adsorption of copper from cyanide solution onto activated carbon increases as the pH and the concentration of free cyanide are lowered, i.e. the loading increases as the degree of cyanide co-ordination and the charge on the complex anion decrease, in the order



The adsorption of aurocyanide onto carbon is accompanied by a shift in the equilibrium pH of the solution from between 5 and 6 to between 10 and 11, depending on the extent of loading. This could be due to the release of either  $\text{OH}^-$  or  $\text{HCO}_3^-$ . There is no shift in pH when  $\text{Hg}(\text{CN})_2$  is adsorbed.

The reduction potential of most commercial activated carbon products lies between 0,10 and 0,40 V. This is sufficiently low for the reduction of the gold chloride complex  $\text{AuCl}_4^-$  to the metal ( $E^\circ = 1,002$  V) but not for the reduction of the aurocyanide complex ( $E^\circ = -0,57$  V). Nevertheless, a correlation has been observed between the loading capacity of the carbon for gold cyanide and its reduction potential, although the correlation for aurocyanide is not as well defined as it is for  $\text{AuCl}_4^-$ .

Oxidation of the surface functional groups of activated carbon with, for example, chlorine or nitric acid, results in a marked decrease in its capacity for gold cyanide and gold chloride.

The capacity of carbon for gold cyanide is greater in an aerated or oxygenated solution than in a solution through which nitrogen is bubbled.

The nitrogen content of carbons loaded with gold from aurocyanide solution is reasonably consistent with the presence of  $\text{Au}(\text{CN})_2^-$ , at gold loadings of lower than  $30 \text{ kg t}^{-1}$ . At higher loadings, the nitrogen-to-gold stoichiometry is somewhat lower than 2.

The gold-loading capacity of activated carbon decreases with increasing temperature.

The adsorption of aurocyanide onto activated carbon is a reversible pro-

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cess in which the equilibria between the concentrations of gold in solution and on the carbon are equal, whether arrived at from above or below. There can be a degree of kinetic hysteresis, however, for the reasons outlined in the section above.

In general, an anion need not be a complexing agent for gold in order to displace the gold from the carbon. For example, gold that has been fully loaded onto the carbon from cyanide solution can be completely stripped with hot sodium hydroxide, and appears in solution as the aurocyanide anion.

The rate of elution is retarded by the addition of salts to the eluate, and enhanced by increases in the temperature or the addition of polar organic solvents such as methanol, ethanol, acetone, or acetonitrile to the eluate.

*Mechanism of adsorption.* Factors that affect the kinetics of adsorption are the hydrodynamic conditions in the adsorption stages, the particle-size and pore-size distribution of the carbon, the viscosity and density of the solution or pulp in contact with the carbon, and the presence of species that can adsorb onto and poison carbon (Fleming and Nicol, 1984). These factors would have the greatest influence on the efficiency of gold extraction in the initial stages of the adsorption process. Factors that influence the equilibrium loading capacity are the pH of the solution in contact with the carbon, ionic strength, temperature, and the concentration of free cyanide (Fleming and Nicol, 1984), and these factors will have an influence on plant performance only if the loading of the gold on the carbon is allowed to approach its equilibrium isotherm.

The various mechanisms of gold adsorption from cyanide solution that have been proposed in the literature generally fall into one of the following categories:

- the reduction of  $\text{Au}(\text{CN})_2^-$  to metallic gold,
- the adsorption of  $\text{M}^+ \text{Au}(\text{CN})_2^-$  ion pairs,
- the electrical double-layer adsorption of  $\text{Au}(\text{CN})_2^-$  and cations onto a charged surface, with partial reduction of the  $\text{Au}(\text{CN})_2^-$  to cluster-type species, or
- the adsorption of  $\text{Au}(\text{CN})_2^-$ , with subsequent degradation to the insoluble  $\text{AuCN}$  species.

In terms of these mechanisms, gold is present on the carbon surface in one or more of the following forms:

- aurocyanide,  $\text{Au}(\text{CN})_2^-$  (valency 1),
- gold cyanide,  $\text{AuCN}$  (valency 1),
- a cluster compound,  $\text{Au}_x(\text{CN})_y$  (valency 0 to 1), or
- gold metal,  $\text{Au}$  (valency 0).

The presence of sub-stoichiometric gold species  $\text{Au}$ ,  $\text{AuCN}$ , or  $\text{Au}_x(\text{CN})_y$  on the loaded carbon is countered by the observation that gold can be eluted from carbon with sodium hydroxide, and appears in the eluate as aurocyanide. Moreover, it is significant that it is possible to partially elute carbon with sodium hydroxide even after treatment of the loaded carbon

in boiling hydrochloric acid for several hours. These conditions would normally be more than adequate for the decomposition of aurocyanide to gold cyanide and the liberation of hydrocyanic acid (Equation 15.2). The fact that this does not occur, or occurs only very slowly, when aurocyanide is loaded onto carbon suggests that the carbon stabilizes the aurocyanide under acidic conditions, probably as the acid,  $\text{HAu}(\text{CN})_2$ . In addition, the thermodynamic evidence tends to counter mechanisms in which gold is reduced to a valency of less than 1. Analyses of carbons with high gold loadings have indicated a ratio of N to Au of less than 2. This suggests some chemical change but, under the sort of loading conditions typical of CIP operations, the weight of evidence favours a mechanism in which aurocyanide is adsorbed without chemical change. Moreover, the sensitivity of the adsorption mechanism to temperature and to the concentration of cations in solution suggests that adsorption does not occur by simple coulombic ion exchange. This is supported by the fact that a neutral molecule such as  $\text{Hg}(\text{CN})_2$  competes very effectively with  $\text{Au}(\text{CN})_2^-$  for adsorption sites on the carbon, and that cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are co-extracted with aurocyanide. These are phenomena that would not normally be associated with ion exchange processes, but are more consistent with a mechanism in which aurocyanide is adsorbed as an ion pair of some sort. The evidence suggests that, at high pH, aurocyanide is adsorbed predominantly as an ion pair of the type  $\text{M}^{n+}[\text{Au}(\text{CN})_2^-]_n$ , (where M is Na, K, Ca, or Mg, etc.), whereas, at low pH, the predominant adsorbing species is the acid,  $\text{H}[\text{Au}(\text{CN})_2]$ . Moreover, the strong dependence of gold adsorption on the pH of the solution indicates that  $\text{H}[\text{Au}(\text{CN})_2]$  is adsorbed more strongly than  $\text{M}^{n+}[\text{Au}(\text{CN})_2^-]_n$ . A mechanism by which both  $\text{H}[\text{Au}(\text{CN})_2]$  and  $\text{M}^{n+}[\text{Au}(\text{CN})_2^-]_n$  are adsorbed simultaneously over a fairly wide pH range would explain the shift in pH that accompanies the adsorption of aurocyanide from neutral solutions, and would also explain the fact that the ratio of  $\text{M}^{n+}$  to Au on the loaded carbon is generally lower than the stoichiometric amount. Such a mechanism is reasonable in view of the fact that the thermodynamics of adsorption on to carbon are more favourable for neutral compounds than for charged species. Examples include the adsorption of mercury (McDougall *et al.*, 1980) and copper (Fleming and Nicol, 1984) from cyanide solution, and the adsorption of molybdenum from acid solution (De Wet, 1985). On this basis it would be predicted that  $\text{H}[\text{Au}(\text{CN})_2]$  will be adsorbed more strongly onto carbon than  $\text{Au}(\text{CN})_2^-$ , and it is likely that the favourable thermodynamics of this interaction will permit the uptake of protons from solution and the formation of  $\text{H}[\text{Au}(\text{CN})_2]$  at higher pH values than might normally be predicted for this reaction.

It is likely that future significant advances in the understanding of this mechanism will be made only as a result of the successful application of direct physical techniques such as X-ray diffraction and infrared spectroscopy.

(b) *The adsorption of gold from leach liquors other than cyanide*

Alternative lixiviants for gold are becoming increasingly important in most gold-producing countries and, since activated carbon is likely to play an in-

tegral part in any process for the recovery of gold in the future, the loading and stripping characteristics of these gold compounds with respect to carbon will need to be studied in detail. One of the earliest producers to use this technology is the New England Antimony Mine in Australia, which recovers gold by thiourea leaching and carbon extraction (Hisshion and Waller, 1984). Techniques for the elution of gold have not been developed, however, and the carbon is burnt so that the gold can be recovered.

The standard reduction potentials for a number of alternative lixiviants are shown in Table 15.2, where they are compared with data for the cyanide system. On the basis of these reduction potentials, one would predict that activated carbon with a reduction potential of 0,10 to 0,40 V (McDougall *et al.*, 1980) would readily reduce the gold chloride and thiocyanate complexes on the carbon surface to the metallic state whereas the gold-thiourea complex would be a borderline case, and would probably be reduced to the metal only at thiourea concentrations lower than about 0,1 M. The gold-thiosulphate complex would probably be too strong to be reduced by carbon.

Recent unpublished results from the laboratory at Mintek indicate, in fact, that both the gold thiourea and gold thiocyanate complexes are adsorbed onto carbon without chemical change, from typical leach solutions. Analysis of loaded activated carbons for sulphur and gold indicates that the ratio of these two elements is, over a wide range of loading conditions, close to the theoretical value of 2 that would be expected for adsorption of the complex ions,  $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$  and  $\text{Au}(\text{SCN})_2^-$ , without chemical change. Moreover, the adsorption of the gold thiourea complex on carbon is generally enhanced by the presence of anions in solution whereas the adsorption of  $\text{Au}(\text{SCN})_2^-$  is enhanced by the presence of cations in solution, which indicates that these two species are adsorbed onto carbon by a similar ion-pair mechanism to that postulated for aurocyanide. The fact that these two ions, which are relatively unstable compared with aurocyanide, are not reduced to the metal by activated carbon is further evidence that the very stable aurocyanide ion is unlikely to be reduced.

### (c) *Elution of gold from carbon*

Since the adsorption of gold cyanide onto activated carbon is a thermodynamically reversible process, chemical and physical factors that inhibit adsorption will enhance elution, and those that enhance adsorption will inhibit elution. A number of these factors are utilized in elution on all industrial CIP plants.

The most important factor is temperature, since the kinetics (activation energy  $66,5 \text{ kJ mol}^{-1}$ ) and the thermodynamics (exothermic heat of reaction  $40 \text{ kJ mol}^{-1}$ ) of elution improve with increasing temperature. All CIP elution plants operate at elevated temperature, and the modern trend is towards elution at temperatures in excess of  $100^\circ\text{C}$ , with the use of pressurized equipment.

Another important factor is the influence of ionic strength on the performance of all CIP elution plants. The fact that the rate of elution increases with increasing anion concentration but decreases with increasing cation con-

centration means that the rate of elution passes through a maximum as the concentration of the eluting salt (NaCN, for example) is increased. Optimum performance is therefore achieved at the concentration of eluting salt that corresponds to this maximum, but there are complicating factors. One of these is that the anion that gives the best results, viz. the cyanide ion, decomposes fairly rapidly at elevated temperatures (40% in 6 hours, 90% in 24 hours at 95°C). This effect is best minimized by the addition of the cyanide in increments throughout the elution cycle rather than in one dose at the start. A second complication arises in the electro-elution process, in which gold is continuously extracted from the eluate by electrolysis before the eluate is recycled back to elution. The requirements for good electrowinning efficiency, especially with regard to the ionic strength (conductivity) and the recirculating flowrate of the eluate, are generally quite different from the requirements for good elution efficiency, and a measure of compromise is necessary.

In seeking to overcome some of these obstacles, the Anglo American Research Laboratory (AARL), which developed the AARL elution method (Davidson and Duncanson, 1977), has moved from a continuous to a batch operation in which the carbon is first soaked in a hot concentrated solution of sodium hydroxide and sodium cyanide and then treated with hot deionized water to elute the gold. The water is passed through the column only once, and the rate of elution is sufficiently fast for good elution efficiency to be achieved with reasonably small volumes of water. The conductivity of the eluate is too low for effective electrolysis unless the pre-soak solution is combined with the eluate after elution. Alternatively, this method is particularly suited to different methods of gold recovery such as chemical reduction (zinc cementation), which allows a portion of the pre-soak solution to be re-used several times, thus conserving the chemical in that solution. This approach has been adopted on several plants.

Another factor that can be utilized in enhancement of the rate of elution is the catalytic effect of polar organic solvents such as acetonitrile, acetone, methanol, and ethanol. This effect is attributed to an increase in the activity of the cyanide ion and a decrease in the activity of the aurocyanide ion in polar solvents relative to the situation in water (Tsuchida *et al.*, 1984).

It was shown recently in laboratory tests at Mintek that carbon loaded from either gold-thiourea or gold-thiocyanate solution can be eluted effectively with sodium sulphide or sodium cyanide solution, and that the rate of gold elution with sodium cyanide is enhanced by addition of polar solvents such as acetone or ethanol. Reasonable rates of elution can, in fact, be achieved even at ambient temperatures and pressures and it is likely that future process technology for these alternative leaching systems will incorporate carbon elution rather than the measures employed at the New England Antimony Mine.

### 15.3.2.2 *The ion-exchange process*

#### (a) *Principles*

Modern synthetic ion-exchange resin consists of an inert polymeric hydrocarbon matrix (usually of polystyrene cross-linked with divinyl benzene) to which

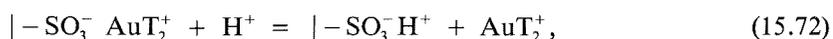
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functional groups are chemically attached. The polymer matrix is a three-dimensional network that swells in contact with aqueous solutions, absorbing water and allowing ions present in the aqueous solution to diffuse through the resulting gel to the sites of the active groups.

The active groups can be anionic or cationic in character, and the interactions between these groups and cations or anions in solution are almost invariably coulombic or electrostatic in nature. The rates of the exchange reactions are therefore high, reversible, and generally diffusion-controlled, and the selectivity of the resins for one ion over another is predominantly a function of the size, charge, and polarizability of the ions.

The active groups in anion-exchange resins are either quaternary ammonium groups for strong-base resins, or primary, secondary, or tertiary amines for weak-base resins. The active groups in cation-exchange resins are either carboxylic (weak) acid or sulphonic (strong) acid. Strong-acid and strong-base resins are completely ionized in the pH range 2 to 12, and exhibit maximum ion-exchange capacity under these conditions. Weak-acid resins are ionized only at  $\text{pH} > 5$ , and weak-base resins at  $\text{pH} < 9$ . This property of weak-base resins can be a limitation in the processing of gold.

As shown in Table 15.1, gold in aqueous solutions of hydrometallurgical interest is generally present as an anionic complex. Consequently, anion-exchange resins are more important than cation-exchange resins in the field of gold metallurgy, and will be dealt with in more detail. One important exception is the aurous thiourea complex, which has a single positive charge (thiourea being a neutral ligand) and is strongly extracted from aqueous solution by cation-exchange resins. The use of thiourea in the leaching of gold ores is gaining momentum overseas and could conceivably become important in South Africa in the future. The thiourea leaching reaction takes place in acid solution ( $\text{pH} 1$  to  $2$ ), and therefore strong-acid resins are required for good extraction efficiency. Since the oxidant is generally the ferric ion (although ozone and peroxide are also effective), ferric and ferrous cations are present in solution in considerable excess. However, strong-acid resins are fairly selective for the aurous thiourea cation over iron cations, and good extraction and separation of gold is possible (Becker *et al.*, 1983). The extraction by strong-acid resins is so powerful, in fact, that desorption with acids according to the equation



(where T is  $\text{NH}_2\text{CSNH}_2$ , and  $|-$  represents the organic matrix), is incomplete even at high concentration of acid (Becker *et al.*, 1983). Experience with the technology of anion-exchange resins indicates that the elution of cation-exchange resins will probably be most effective either coupled with continuous electrolysis of gold or in the presence of mixed aqueous-organic solvents.

Because of the importance of the cyanidation process in gold metallurgy, anion-exchange resins have received far more attention than cation-exchange resins. Strong-base resins extract aurocyanide anions (and other singly charged anionic gold complexes) according to the equation

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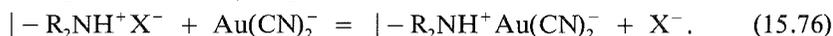


The equilibrium in Equation (15.73) is defined as the mass-distribution ratio,

$$K_{SB} = \frac{\overline{[Au(CN)_2^-]}[X^-]}{[Au(CN)_2^-]\overline{[X^-]}} \quad (15.74)$$

(where bars denote ions in the resin phase), the position of which is determined by the relative affinity of the resin for the counter-ion,  $Au(CN)_2^-$ , and the co-ion,  $X^-$ .

Weak-base resins are in the free-base (non-ionized) form at pH values higher than 9 to 10 and, under these conditions, possess no ion-exchange characteristics. In neutral or acidic solution the amine is protonated, and ion-exchange occurs according to the following equations:



The equilibrium constant for reaction (15.76) is written

$$K_{WB} = \frac{\overline{[Au(CN)_2^-]}[X_{WB}^-]}{K_a[Au(CN)_2^-]\overline{[X^-]}} \quad (15.77)$$

where  $K_a$  is the equilibrium constant for the resin protonation reaction (15.75). In this case the value  $K_{WB}$  is influenced not only by the affinity of the resin for the respective anions, but by the pH of the solution, and this is the only significant difference between strong- and weak-base resins.

The  $pK_a$  of weak-base resins is determined both by the basicity of the amine group and by the nature of the anion in solution. The strength of the ion pair formed between the anion and the active group on the resin increases with the charge and the polarizability of the anion, and the driving force for ion pair formation permits uptake of the proton from far more alkaline solutions when strong ion pairs are formed. For example, the strong ion pair formed between an amine and the large, highly polarizable aurocyanide anion yields a  $pK_a$  of about 9 to 10 (Fleming and Cromberge, 1984a), whereas the  $pK_a$  of the same resin in chloride solution is some 2 log units lower. This has important implications in the extraction of gold from cyanide leach liquors, which normally have pH values between 10 and 11.

An important property of an anion-exchange resin is its selectivity for aurocyanide, because many complex cyanide anions and other anions are usually present with aurocyanide in cyanide leach liquors, and the competitive extraction of these anions can have a profound influence on the efficiency of gold extraction. The competitive ion-exchange reactions that take place can be represented by the general equation



(where the anion A has a negative charge of  $y$  and the anion B has a negative

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Table 15.3. Selectivity coefficients,  $k_{\text{Au(CN)}_2^- / \text{A}^-}$  of  $\text{Au(CN)}_2^-$  against various anions,  $\text{A}^-$ , on the strong-base resin Amberlite IRA 400 (after Aveston *et al.*, 1958).

Anion A	$k_{\text{Au(CN)}_2^- / \text{A}^-}$
$\text{Co(CN)}_6^{3-}$	$8 \times 10^9$
$\text{Fe(CN)}_6^{3-}$	$6 \times 10^9$
$\text{F}^-$	$5,5 \times 10^3$
$\text{Cl}^-$	$6,9 \times 10^2$
$\text{CN}^-$	$3 \times 10^2$
$\text{Ni(CN)}_4^{2-}$	$2,5 \times 10^2$
$\text{CNS}^-$	9,6
$\text{Ag(CN)}_2^-$	5,8
$\text{ClO}_4^-$	4,6
$\text{Au(CN)}_2^-$	1,0
$\text{MnO}_4^-$	0,53

charge of  $z$ ). The selectivity of the resin for anion B over anion A is defined by the coefficient

$$k_{\text{B/A}} = \frac{[\text{B}]^y [\text{A}]^z}{[\text{A}]^z [\text{B}]^y}, \quad (15.79)$$

which has the same form as the equilibrium constant in Equation (15.74).

Table 15.3 shows values of the selectivity coefficient of a strong-base resin for aurocyanide over various other anions that are commonly present in cyanide leach liquors. The concept of a selectivity coefficient is useful for theoretical studies, but is unfortunately of limited value when the relative extractions of anions are predicted. In fact, the predictions that might be made intuitively on the basis of selectivity coefficients bear little relation to what is found in practice, as illustrated in Figure 15.17. The isotherms for various metals shown in Figure 15.17 were obtained by the equilibration of a pregnant cyanide solution from a gold plant with a commercial strong-base resin. It could have been predicted, on the basis of the selectivity coefficients in Table 15.3, that an anion-exchange resin would extract gold preferentially from a solution containing cobalt(III) and nickel, whereas Figure 15.17 shows that nickel and cobalt are preferentially extracted.

From a practical point of view, a far more valuable concept is the separation factor. This is defined as

$$\alpha_{\text{B/A}} = \frac{[\text{B}] [\text{A}]}{[\text{A}] [\text{B}]}, \quad (15.80)$$

which is simply the quotient of the concentration ratios of the two counterions in the resin phase and in solution. The numerical value of the dimensionless separation factor is not influenced by the choice of concentration units or by the charge on the anion, but it does vary with the concentration of anions A and B in solution.

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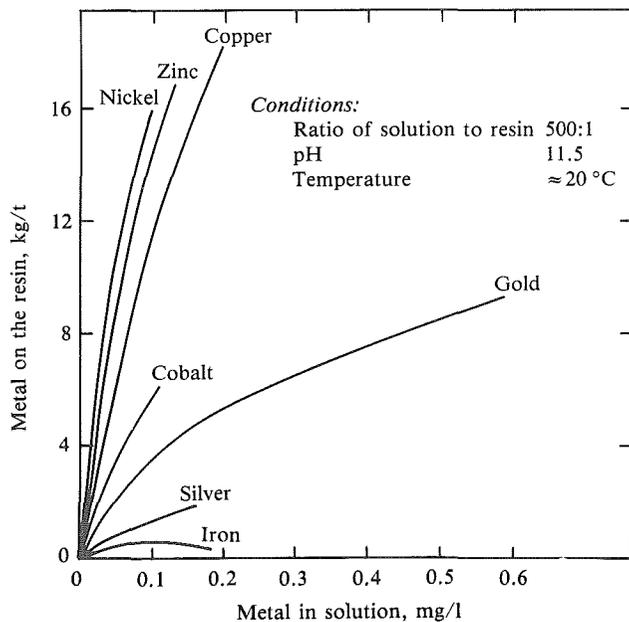


Figure 15.17. Equilibrium loading of various metal cyanide complexes from a Grootvlei pregnant solution onto a strong-base resin (A101 DU) (after Fleming and Nicol, 1984).

Since the preference of the resin for one anion over another is a function mainly of the properties of the anion, there is not much that one can do to influence the selectivity in favour of aurocyanide. However, it has been shown (Clifford and Weber, 1983) that the selectivity of anion-exchange resins for monovalent anions over polyvalent anions is a function of the distance that separates the fixed charges on the resin matrix. The uptake of a divalent anion requires the presence of two closely spaced positive charges, whereas no such constraint exists for monovalent anions. On this basis, the proportion of sites having suitable locations for the adsorption of multivalent ions will decrease as the capacity of the resin decreases or, in the case of weak-base resins, as pH is increased. The influence of this phenomenon on the selectivity of anion-exchange resins for aurocyanide over multivalent metal cyanide complexes was first reported nearly thirty years ago (Aveston *et al.*, 1958). Table 15.4 shows that the application of this theory results in greatly improved separation factors between aurocyanide and a range of multivalent metal cyanide anions on a weak-base resin.

The data for two weak-base resins show that the separation factor between aurocyanide and the various multivalent metal cyanide anions increases by a factor of ten to one hundred upon increasing the pH value of solution from 6 to 11. In contrast, the separation factors on a strong-base resin are largely unaffected by pH, as might be expected. It is also interesting to note

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Table 15.4 Separation factors\* between aurocyanide and various metal cyanide anions on two weak-base resins (A7, Duolite International; IRA 93, Rohm and Haas) and one strong-base resin (A101 DU, Duolite International). Concentration of metal in solution  $10^{-4}$  M.

Anion B	${}^{\circ}\text{Au}(\text{CN})_2^- / \text{B}$					
	A7		IRA 93		A101 DU	
	pH6	pH11	pH6	pH11	pH6	pH11
$\text{Ag}(\text{CN})_2^-$	7,6	7,9	12,3	15,4	8,8	8,6
$\text{Ni}(\text{CN})_4^{2-}$	1,9	5,9	0,7	19,0	1,1	0,9
$\text{Cu}(\text{CN})_3^{3-}$	1,8	35,5	3,3	32,3	8,2	4,9
$\text{Co}(\text{CN})_6^{3-}$	0,8	71,0	0,9	6,3	1,6	0,8
$\text{Fe}(\text{CN})_6^{3-}$	0,7	6,2	0,8	13,5	2,0	4,4

\* Calculated from data reported by Fleming and Cromberge (1984a).

that the separation factor between aurocyanide and the only other monovalent anion in solution, silver cyanide, is unaffected by a change in pH.

Most weak-base resins have a low and variable concentration of permanently charged functional groups. These pseudo-strong-base groups arise via the cross-linking of adjacent amine groups and have the properties of the quaternary amine groups in a strong-base resin. Russian workers (Laskorin *et al.*, 1977) have observed that certain weak-base resins with a low strong-base content extract gold very selectively from cyanide solutions of high pH, but that the selectivity disappears when the strong-base content exceeds about 20% of the total resin capacity. The mechanism of rejection of the multivalent complex cyanide anions in this situation is presumably also based on charge separation.

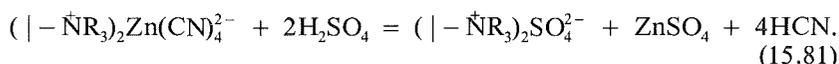
The elution of weak-base resins is achieved most effectively and cheaply by the treatment of the resin with a fairly dilute solution of sodium hydroxide. This shifts the equilibrium in Equation (15.75) to the left-hand side, and restores the amine functional groups to the free-base form. When electrolysis is coupled with elution, 99% of the aurocyanide can be eluted from a weak-base resin with 1 or 2 bed volumes of 0,5 M sodium hydroxide solution in less than 4 hours (Fleming and Cromberge, 1984b). The effectiveness and simplicity of this method is a major factor in favour of the use of weak-base resins in gold metallurgy, but this advantage has to be weighed against the fact that their capacity is low compared to that of strong-base resins, particularly at the pH values (10 to 11) that are usually encountered in cyanide leach liquors.

The elution of aurocyanide from a strong-base resin is more difficult, and is achieved either by ion-exchange mass action, i.e. by the reversal of the equilibrium shown in Equation (15.73), or by the chemical destruction of the aurocyanide anion. Because aurocyanide is so strongly adsorbed, its elution by ion-exchange requires a large excess of the co-ion,  $\text{X}^-$ . Anions such as chloride, bisulphate, nitrate or cyanide can be used, but the rate of aurocyanide elution is extremely slow unless the activity of these anions is increased by, for example, the addition of polar organic solvents such as

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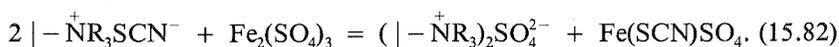
acetone, acetonitrile, or methanol to the eluate. Anions such as thiocyanate and the zinc cyanide complex, on the other hand, compete favourably with aurocyanide, and much higher rates of elution can be achieved. When electrolysis is coupled to elution, either of these anions can elute 99% of the gold under ambient conditions in 6 to 24 hours (Fleming and Cromberge, 1984b).

Because thiocyanate and zinc cyanide themselves load strongly onto anion-exchange resins, the resin must be regenerated before being recycled to adsorption. In the case of the zinc cyanide complex, this is achieved effectively and cheaply by the destruction of the complex with acid (Fleming and Cromberge, 1984b).



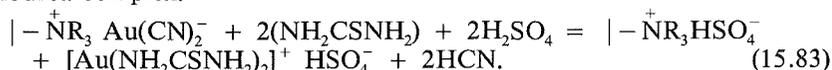
The zinc sulphate and hydrocyanic acid produced in this reaction are collected in alkaline solution so that the zinc cyanide anion can be reconstituted for recycling.

The removal of thiocyanate from a strong-base resin can be achieved effectively by treatment with a ferric salt (Fleming, 1984 and 1985). The cationic complexes  $\text{FeSCN}^{2+}$  and  $\text{Fe}(\text{SCN})_2^+$  are formed, and these are readily displaced from an anion-exchange resin:



Thiocyanate for recycling can be recovered from this solution by the precipitation of the iron from solution as ferric hydroxide. The ferric hydroxide precipitate can then be redissolved in acid and recycled to regeneration. In this way the thiocyanate and ferric ions are conserved in the elution-regeneration cycle (Fleming, 1985). The method is efficient, cheap and non-toxic, and would probably be preferred to the zinc cyanide method in most applications.

The alternative method for the stripping of gold from a strong-base resin involves the chemical conversion of the aurocyanide anion to the aurous thiourea complex:



This method of elution is favoured in the Soviet Union, but suffers from the drawback that the other metal complexes that are co-extracted with aurocyanide during adsorption are generally poorly eluted, necessitating multi-elution procedures. This problem is particularly serious when cobaltcyanide and ferrocyanide are formed since, in acidic solution, they are converted to species that are very difficult to strip from the resin (Fleming and Cromberge, 1984b; Fleming and Hancock, 1979).

### (b) Applications

Although the zinc precipitation process is simple and cheap and the technology is well developed, an anion-exchange concentration and purification step may

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be preferred in certain instances. For example, the chemical composition of the leach liquor occasionally does not lend itself to the quantitative or economic recovery of gold by zinc cementation (e.g. when the concentration of gold is very low or the concentration of impurities is very high), but the major potential application of anion-exchange resins in the processing of gold is in the recovery of aurocyanide direct from the pulp in the RIP process. The filtration and clarification steps are costly components of the conventional gold process, especially with certain ores that are not amenable to filtration, and it is likely that the RIP process would offer significant cost advantages in most applications. In this regard, the RIP process is no different from the CIP process, but in some situations RIP may be preferred to CIP, and these are discussed below.

The use of anion-exchange resins for the extraction and concentration of aurocyanide in dilute solutions or pulps was first proposed in the early 1950's, and a number of experimental studies were carried out at that time (Hussey, 1949; Burstall *et al.*, 1953; Burstall and Wells, 1955). Since then, further work has been done in all the major gold-producing countries (Davison *et al.*, 1961; Demidov *et al.*, 1967; Tataru, 1974; Stamboliadis *et al.*, 1978), and a recent study in South Africa (Fleming and Cromberge, 1984a, 1984b and 1984c) concluded that, in many cases, resin-based processes for the recovery of gold are probably superior to carbon-based processes from economic, chemical, and metallurgical points of view. This would seem to be confirmed by reports emanating from the Soviet Union, since a 1978 article indicates that one of the largest gold mines in the U.S.S.R. is using an anion-exchange resin for the extraction of aurocyanide by an RIP process (Anon., 1978). This is believed to have been the world's first application of RIP to the extraction of gold, although the article states that 'RIP is now used widely for gold extraction in the Soviet Union'. The questions that remain to be answered, before the large-scale application of RIP to the recovery of gold becomes a reality, are all related to the engineering of RIP on a large scale. For example, the mean particle size of resins is smaller than that of carbon, which means that interstage screening in RIP will have to be carried out at a finer cut than in CIP (probably 0,60 mm in RIP as against 0,85 mm in CIP). This gives justifiable cause for concern, since interstage screening has tended to cause bottlenecks on most large CIP plants. Probably of lesser concern is the question of resin life in an RIP circuit, since the available literature on the subject (Laskorin *et al.*, 1978; Hosking, 1984) indicates that resin losses are likely to be somewhat lower than carbon losses.

RIP will probably make its greatest impact in those areas where the treatment of pulp by CIP poses problems. For example, it has been shown that RIP is far less responsive to the presence of poisons in the pulp than CIP. These poisons include organic compounds such as flotation reagents, solvents and lubricants, and inorganic compounds such as hematite, calcium carbonate, shales, and clays. Each of these species retards the adsorption of gold onto carbon, but apparently has little effect on the extraction properties of resin.

It is likely that operators treating small tonnages (<20 kt per month)

will find RIP an attractive alternative to CIP. The capital costs for a carbon elution-regeneration plant are high and generally cannot be justified on small CIP plants. In these cases gold is recovered by incineration of the loaded carbon, which imposes high operating costs on the process. RIP, with its potential for relatively inexpensive elution and regeneration (in regard to capital and operating costs), would be a viable alternative in these situations.

In the South African context, a potential advantage of resins over carbon is that they offer a means for the simultaneous recovery of gold and uranium. Gold and uranium are, in fact, co-extracted on many uranium plants in South Africa where, more by accident than design, uranium plants are often used to scavenge gold that would normally be lost as a soluble residue from the gold plant. This is because aurocyanide is relatively stable in the uranium-leaching circuit, and both gold and uranium are present in solution as anionic complexes. Various possible options for the translation of this interesting chemistry into a viable process have been explored over the years (Anglo American Corporation, 1977; Fleming and Cromberge, 1984d).

In addition, a number of uranium mines in South Africa have stockpiles of old, discarded strong-base resin that has lost its ion-exchange capacity as a result of poisoning or degradation. Although the value of the gold on the resin often exceeds the value of the resin itself, recovery of the gold by incineration of the resin has never been practical because of the very toxic and noxious fumes that are produced. Consequently, the resin has been stockpiled pending the development of more suitable gold-recovery technology. One example of such a stockpile is the resin at the Stilfontein mine, which was last used in the early 1950's in a fixed-bed uranium plant, and was removed from the circuit owing to extensive poisoning by cobalticyanide. The stockpile contains about 100 t of resin with an average gold content of  $900 \text{ g t}^{-1}$ ; a plant for the recovery of the gold from this resin was commissioned in 1984. The method adopted, which is based on technology developed at Mintek (Fleming, 1985), involves electro-elution with ammonium thiocyanate, and has enabled gold recoveries of over 90% to be regularly achieved. In addition, cobalt is partially stripped from the resin, and much of the original ion-exchange capacity of the resin is restored after ferric regeneration. This offers the possibility that the resin in this stockpile can be returned to active service.

#### 15.3.2.3 *The solvent-extraction process*

Solvent extraction is a well-established method of separation in extractive metallurgy. This technique was first applied to the extraction of uranium for nuclear purposes in the 1940's, and is currently widely used in the recovery of uranium, copper, zinc, cobalt, nickel, vanadium, tungsten, and molybdenum, as well as in separations involving the platinum-group metals.

The solvent-extraction process involves the transfer of a solute from an aqueous to an organic phase, and the subsequent extraction of the solute back into another aqueous phase under a different set of chemical or physical conditions. For a species present in aqueous solution to be able to pass into an organic phase, it must react with an organic component. Metallic ions

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can occur in aqueous solutions in a variety of forms, either free or as complexes and, in general, only a particular ion, or at most a limited number of these ions, will react with the solvent and be extracted. The distribution of the metal between the two phases will therefore be greatly influenced by the composition of the aqueous phase. The solvent may be a pure organic liquid or, more usually, a solution of an organic reagent in an inert diluent. The organic reagent may undergo association, solvation, or other reactions in the organic phase, and these will also affect the extraction equilibrium.

Solvent-extraction systems can be conveniently classified according to the nature of the reaction involved in the extraction process, of which the following types can be identified.

*Extraction by physical distribution* involves a simple molecular distribution of the solute between the aqueous phase and an inert solvent (i.e. one containing no atoms with electron donor properties). Such a situation arises only for solutes that are poorly solvated in the aqueous phase, and few such systems are encountered in extractive metallurgy.

*Extraction by solvation* involves the replacement by the extractant of some or all the co-ordinated water molecules on a metal cation to form a species that is soluble in the organic phase. Solvating extractants are most characteristically oxygen-containing organic molecule such as ethers, esters, alcohols, ketones, and neutral organophosphorus compounds. This kind of extraction is restricted to neutral species because it is necessary to preserve the electrical neutrality of the phases. The extraction of auric chloride from acid solution (as  $\text{HAuCl}_4$ ) would be one example of such a process (Walker, 1956).

*Extraction by anion exchange* is characterized by the use of a suitable cation for the extraction of an anionic metal compound in the form of an ion pair, after a simple (non-metallic) anion has been exchanged between the organic and aqueous phases in the reverse direction. Often the cationic component of the ion pair is formed by the protonation of a compound of weak basicity, most typically a nitrogen-containing base such as an amine. Alternatively, the cation may be of the quaternary ammonium, phosphonium, or arsenium type. Recovery of gold from cyanide, thiocyanate, or thiosulphate leach liquors would fall into this solvent extraction category.

*Extraction by cation exchange* involves the formation, by a hydrated metal cation or complex metal cation, or an electrically neutral co-ordination complex with the extractant by the displacement of another cation (most commonly a hydrogen ion). The formation of the extractable complex can involve chelation and chemical bonding between the extractant and the metal ion, or it can involve simple electrostatic interaction between an anionic extractant (such as a sulphonic acid) and a metal cation. When the cation displaced from the extractant is a hydrogen ion, the extractability of the metal shows a distinct dependence on the pH value of the aqueous phase. Thus gold could be recovered from a thiourea leach liquor by cation-exchange solvent extraction.

The anion- and cation-exchange reactions that take place in the solvent are the same as those in ion-exchange resins. The major differences between

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the two techniques arise as a result of the difference in the inert supporting matrix, which is an organic liquid such as kerosene in solvent extraction, and a solid organic polymer such as polystyrene in an ion-exchange resin. This difference can give rise to differences in the rates of anion or cation exchange, and also in the order of selectivity of the extractant for various anions and cations but, in general, the metallurgical performance of the two techniques can be expected to be very similar.

The grade or value of the aqueous solution being treated is probably the most important consideration in the choice between resins or solvents for a hydrometallurgical application. Solvent extraction is generally preferred for the treatment of small volumes of high-grade solution, whereas resins are preferred for the treatment of large volumes of low-grade solution. This is because solvent is lost in solvent extraction, and this becomes relatively important with respect to operating costs when large volumes of solution are processed, whereas resins are effectively insoluble in water and therefore do not suffer from this drawback. Another important factor is that resins are able to treat metal solutions containing high concentrations of suspended solids, whereas costly solution clarification steps are indispensable in any solvent-extraction process.

For these reasons, solvent extraction is unlikely to find applications in the large-scale processing of solutions resulting from the cyanidation of low-grade gold ores, although the process could possibly contribute to the processing of high-grade ores or concentrates. Its greatest contribution, however, is likely to be the final purification and refining of concentrated gold solutions resulting from the leaching of materials such as jewellery and electronic scrap, anode slimes, and platinum-group-metal (PGM) concentrates.

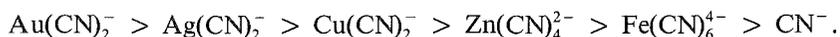
The traditional route for the industrial separation of the platinum-group metals comprises a complicated series of operations based largely on selective precipitations, often of low efficiency (Edwards, 1976). A multitude of solid-liquid separations and recycle operations is required. The poor once-through yield of refined metals results in a high inventory of process intermediates, which is particularly undesirable in view of the high value of the final product. Solvent-extraction methods, with their potential for efficient separations and rapid throughput were found to represent an attractive alternative to established refining procedures, and have been used by several major PGM refiners since the late 1970's. (Edwards, 1979; Cleare *et al.*, 1979; Barnes and Edwards, 1982.)

The existence of the PGM and gold in the form of complex anions in chloride media has been used to advantage in the design of several anion-exchange solvent-extraction processes. The reagents of importance are primary, secondary, tertiary and quaternary amines and these are direct analogues of the weak-base and strong-base resins referred to earlier. Like weak-base resins, the primary, secondary, and tertiary amines undergo protonation reactions, and therefore their activity is also dependent on pH. The extraction of the PGM by amine salts was first reported some thirty years ago (Zeigler and Glemser, 1956). Shortly afterwards, a process for the recovery of the PGM by solvent extraction was patented in the Soviet Union

(Bobikov *et al.*, 1961). The results of pilot-plant operations for the recovery of gold and PGM from copper- and nickel-containing refinery slimes have also been described (Dolgikh *et al.*, 1967), and it is probable that such processes are currently in full-scale commercial use. Further extensive studies by Soviet workers were described in a recent review (Gindin, 1981).

Other solvents that are used for the separation of gold chloride from the PGM include dibutyl carbitol, which is used by Inco (Barnes and Edwards, 1982), and methyl isobutyl ketone, which is used by Matthey Rustenburg Refiners (Reavill and Charlesworth, 1980). In both instances, metallic gold of high purity can be recovered directly from the organic phase by the addition of solutions of oxalic acid, iron(II), or other reducing agents. In addition, the use of dialkyl sulphides for the extraction of gold and palladium from chloride solution has been patented in South Africa (Edwards, 1979) and, in a process employing isodecanol as the extractant (Fieberg and Edwards, 1978), it has been shown that gold can be stripped from the loaded organic phases by contact with water at 50°C. The strip solution produced has a gold content of 50 g l<sup>-1</sup>.

Amines have also been used for the extraction of gold from alkaline cyanide solution and, with trioctylamine, the order of extraction was found (Plaskin and Shivrin, 1963) to be



This order is similar to the order of affinities of ions for anion-exchange resins (Table 15.3). As with weak-base resins, good extraction of aurocyanide by tertiary amines occurs under conditions in which the solutions are so alkaline that a large percentage of the amine is in the unreactive, free-base form, i.e. the driving force for the formation of strong ion pairs permits the uptake of protons by the amine at higher pH values than would be expected for weak ion pairs. For example, the extraction of uranyl sulphate, which forms relatively weak ion pairs with amines, is efficient only at pH values lower than 3 to 4, whereas aurocyanide is extracted efficiently at pH values up to 6 and 7. Nevertheless, the basicity of tertiary amine solvents in aurocyanide solution ( $\text{p}K_a \approx 6$ ) is significantly lower than that of weak-base resins ( $\text{p}K_a \approx 9$ ), and this limits the use of amine solvent-extraction processes for the treatment of gold cyanide. Primary ( $\text{p}K_a \approx 6.5$ ) and secondary ( $\text{p}K_a \approx 7.5$ ) amine solvents are somewhat stronger (Mooiman and Miller, 1983), but are still too weak to extract gold efficiently at pH values that would be compatible with free cyanide in solution ( $\text{p}K_a \approx 7$ ). The need for the pH value to be reduced from about 10, which is normal for cyanide leach liquors, to about 6, which would be necessary for amine solvent extraction, is an added disadvantage.

Recently, Mooiman and Miller (1983 and 1984) showed that the basicity of amine solvents can be increased significantly by the addition of tri-*n*-butyl phosphate (TBP) or other organic phosphorus oxides to the organic phase. They showed that the  $\text{p}K_a$  for the extraction of aurocyanide can be increased from between 6 and 7 to about 10 by the addition of TBP to the organic phase at concentrations in the range 20 to 80% (by volume). The

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Table 15.5. Standard reduction potentials of reductants for precipitation of gold.

Reaction	$E^{\circ}(\text{V})$
$\text{Fe}^{3+} + e = \text{Fe}^{2+}$	0,77
$\text{SO}_4^{2-} + 4\text{H}^+ + 2e = \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0,17
$\text{Sn}^{4+} + 2e = \text{Sn}^{2+}$	0,15
$2\text{H}_2\text{CO}_3 + 2\text{H}^+ + 2e = (\text{COOH})_2 + 2\text{H}_2\text{O}$	-0,39
$\text{BO}_3^{3-} + 7\text{H}_2\text{O} + 8e = \text{BH}_4^- + 10\text{OH}^-$	-0,75

increase in amine basicity was attributed either to solvation of the amine by the modifier or to an increase in the water content of the organic phase. Evidence for the latter effect is the fact that the order of increasing amine basicity in the presence of a range of modifiers parallels the order of increasing solubility in water of the pure modifiers, and is consistent with the fact that the  $\text{p}K_a$  values of amines are generally 2 to 3 orders of magnitude higher in water than they are in organic solvents.

TBP and other donor solvents extract aurocyanide fairly efficiently in the absence of amine by a mechanism that is probably similar to the mechanism of extraction of aurocyanide by activated carbon. Extraction from alkaline solutions (pH 7 to 14) occurs only at high ionic strength, and probably takes place via solvation of the ion pair  $\text{M}^{n+}[\text{Au}(\text{CN})_2]_n^-$ . However, Russian workers (Zvyagintsev and Zakharov-Nartisov, 1960) have shown that aurocyanide, after acidification with hydrochloric, nitric, or sulphuric acid and conversion to  $\text{H}[\text{Au}(\text{CN})_2]$ , can be extracted with donor solvents even from solutions of relatively low ionic strength. They showed that extraction by solvation decreased in the order ethers > esters > alcohols > ketones > aldehydes, and the extraction coefficient decreased in the order hydrochloric acid > nitric acid > sulphuric acid.

### 15.3.3 Chemical precipitation

The reduction of dissolved gold to the metallic state can be achieved by the use of various (non-metallic) chemical reducing agents. For any reductant to be effective, the standard reduction potential must be lower than that of the corresponding half-reaction for the reduction of the gold complex. The reduction potentials of several reductants that are used or are potentially useful are given in Table 15.5.

Comparison of these data with those in Figure 15.15 for the reduction of the gold(III) and gold(I) complexes of various ligands, shows that all the reductants should be effective in the precipitation of gold from chloride solutions and that all, except ferrous ions, should be useful if the gold is leached with thiourea or thiocyanate. On the other hand, it can be expected that gold in solution as the thiosulphate complex will be reduced by only oxalic acid or borohydride, while gold in the form of the aurocyanide ion can be precipitated only by the borohydride ion.

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These predictions are generally borne out in practice, the reduction of gold from chloride solutions by ferrous ion, sulphur dioxide, or oxalic acid being the most widely applied, notably in the refining of gold. The precipitation of metallic gold from thiourea or cyanide leach liquors by chemical reductants is not used commercially, because metallic reductants such as zinc dust are less expensive and more effective than reagents such as sodium borohydride. It is interesting to note, however, that the latter reductant can be used for the precipitation of gold from concentrated solutions such as those produced by the elution of activated carbon or by the intensive cyanidation of gravity concentrates. Unpublished work at Mintek has shown that 90% of the gold (and silver) in a CIP eluate with a gold content of  $250 \text{ g t}^{-1}$  can be precipitated as an easily flocculated gold powder by the use of a ten-fold excess of sodium borohydride at  $80^\circ\text{C}$ . The loss of borohydride by decomposition, which is catalysed by the fine particles of activated carbon in the eluate, was identified as the major practical problem in the use of this reagent.

Finally, mention should be made of the precipitation of gold as insoluble  $\text{AuCN}$  by the acidification of aurocyanide solutions. Such solutions are metastable at low pH values (below about 3) because the precipitation of  $\text{AuCN}$  by the reaction



is relatively slow. However, in the presence of other metal cyanide complexes, notably those of copper, precipitation is rapid, and this has formed the basis of a patent (Sorensen and Davidson, 1981) for the recovery of gold from CIP eluates.

### 15.3.4 Electrowinning

Electrolysis was first used for the recovery of gold on the Witwatersrand in 1894 (Johnson, 1912). For some years the Siemens-Halske electrolytic process competed with zinc cementation as the preferred method for the recovery of gold, but was finally displaced by cementation in 1899, owing to the marked improvements in recovery that were obtained by the use of zinc dust.

The development of the CIP process (Zadra *et al.*, 1952) rekindled interest in electrowinning, and a number of new electrolysis cells were designed. Although these cells have much higher space-time yields than the Siemens-Halske electrolytic cell, almost no improvement in the final concentration of gold in the barren solution (typically  $0.2$  to  $1 \text{ g t}^{-1}$ ) has resulted. For this reason electrolysis can be considered as a technical alternative to cementation only when some method for concentration of the gold, such as the adsorption of soluble gold onto carbon or resins, or the use of gravity concentration prior to leaching (Davidson *et al.*, 1978), is employed prior to the recovery stage.

#### 15.3.4.1 Cell design

The recovery of any electroactive species by electrodeposition is measured in terms of a single-pass extraction efficiency,  $E$ , where

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$$E = 1 - C_{\text{out}}/C_{\text{in}},$$

where  $C_{\text{in}}$  and  $C_{\text{out}}$  are the concentrations of electroactive species entering and leaving the electrowinning cell respectively. As the electrolyte has a finite residence time in the electrowinning cell,  $E$  can be increased only if the rate of deposition,  $R$ , is increased. The maximum possible value of  $R$  is given by the equation

$$R = kAC,$$

where  $k$  is the mass-transport coefficient,  $A$  the electrode area, and  $C$  the concentration of reducible species. The value of  $E$  can therefore be increased by an increase in the available cathode area and/or the mass-transport coefficient.

In terms of operating simplicity, an increase in  $E$  is most readily implemented by increase of the electrode area. In the Siemens-Halske cell this was achieved by the installation of a large number of planar lead foil cathodes (Clevenger, 1915). Although a high value of  $E$  was attained, the cell was extremely large in relation to the mass of gold recovered (i.e. the space-time yield was very low). In a later development of the cell, the lead was cut into shavings that were packed into the space between the anodes (Clevenger, 1915) in order to increase the cathode area in the smallest possible volume. It is most probable that this development constitutes the first industrial use of what is now termed a 'packed-bed' reactor.

The Zadra (Zadra *et al.*, 1952; Elges *et al.*, 1984), AARL (Davidson *et al.*, 1978; Young *et al.*, 1984) and Mintek (Paul *et al.*, 1983; Paul, 1985) electrowinning cells are modern examples of packed-bed electrowinning cells that are commercially available for the recovery of gold. Very high surface areas are attained in these cells by the use of steel wool as the cathode material. The development of electrowinning cells for the recovery of gold in the Soviet Union has also followed the approach involving increase of the surface area. This increase is achieved by the use of fibrous carbon-graphite, woven into cloths, fabrics, or felts, as the cathode material (Maslii *et al.*, 1976; Varentsov *et al.*, 1984).

Many attempts have been made to improve the space-time yield of electrowinning cells by improvement of the mass-transfer characteristics of the reactor (Marshall and Walsh, 1985). The fluidized-bed reactor (Goodridge, 1977) was developed in an attempt to increase both the mass-transport coefficient and the surface area of the reactor. Very few of these designs have managed to overcome the problems associated with scale-up from the laboratory to industrial units (Marshall and Walsh, 1985), and none has found application in the gold-mining industry. The rotating tubular bed reactor (Kammel and Lieber, 1981) and the Chemelec cell (Tyson, 1983) are used for the recovery of precious metals from electroplating rinse water. The application of the Chemelec cell for the recovery of gold from eluates has been suggested (Tomlinson, 1984).

All packed-bed electrowinning cells can be classified into two broad groups according to their design. The cells in the first group operate with the direction of the flow of electrolyte at right angles to the direction of the

## THE EXTRACTIVE METALLURGY OF GOLD

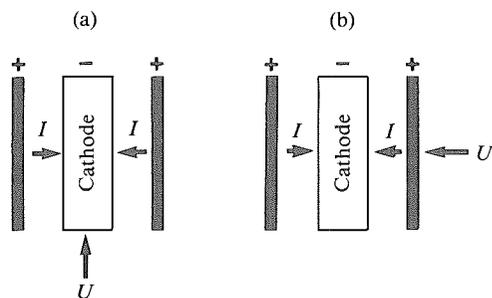


Figure 15.18. Schematic representation of packed-bed electrodes with the flow of solution,  $U$ , at right angles (a) and parallel (b) to the flow of current,  $I$ .

flow of current (*a* of Figure 15.18). Those in the second group operate with parallel flows of solution and current (*b* of Figure 15.18). Although the Zadra and AARL cells incorporate a cylindrically shaped cathode surrounded by a single tubular anode, these cells belong to the first group. Cells of Soviet and Mintek design (i.e. a rectangular tank containing alternately spaced anodes and cathodes positioned across the width of the tank) belong to the second group.

The major design problem in the construction of an electrowinning cell with the flows of current and solution at right angles to each other is the elimination of any path that would enable the solution to by-pass the cathode bed. Inspection of Figure 15.18*a* reveals that the vertical flow of solution can freely enter the gap between the anode and the cathode, thus by-passing the cathode bed. The problem can be alleviated if the electrolyte is pumped down a feeder tube that is positioned vertically in the centre of the cathode bed and has orifices along its entire length that allow the electrolyte to be distributed horizontally. This technique (or a modified version of this technique) is employed in both the Zadra and AARL cells. A further improvement can be made by the use of a cation ion-exchange membrane to separate the anode and cathode compartments (a feature of the AARL cell), thus restricting the flow within the cathode compartment.

However, it is evident that by-passing of the cathode is a feature inherent in this type of packed bed design. The result is low single pass extractions in relation to the cathode volume and to the flow velocity through the cathode.

In addition to the problem of the flow of electrolyte 'mechanically' by-passing the cathode bed, 'electrical' by-passing of the electrolyte within the bed must be prevented. Electrical by-passing occurs as a result of the finite conductivity of the electrolyte, which causes the electrode potential to become more positive towards the centre of the packed bed. The shift in potentials occurs simply because the difference in potential between any two points in the cathode is equal to the current flowing across those points multiplied by the effective resistance of the electrolyte. The positive increase in poten-

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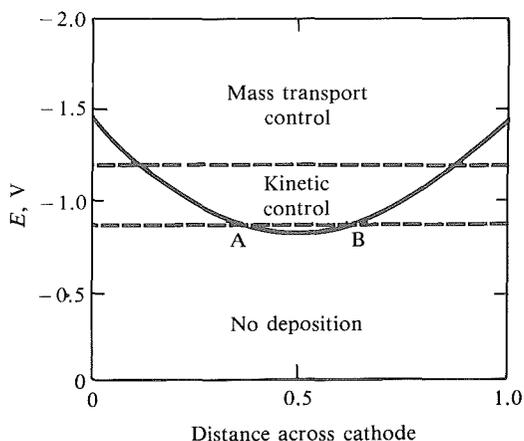


Figure 15.19. Typical distribution of potential across a packed-bed cathode of unit thickness.

tials therefore increases with decreasing conductivity of the electrolyte. A typical potential gradient across the packed-bed cathode of unit thickness is shown in Figure 15.19.

The deposition of gold from an alkaline cyanide electrolyte does not begin until a potential of about  $-0,7$  V is attained (the exact potential depends on the composition of the solution, temperature, etc.). Over the potential range  $-0,7$  to  $-1,1$  V the rate of deposition is kinetically controlled, but becomes mass-transport controlled at potentials more negative than  $-1,1$  V. It is evident from Figure 15.19 that solution passing vertically through the region of the bed marked *AB* will not be subjected to potentials that are sufficiently negative to cause the gold to be deposited. It is this inactive area of the packed bed that accounts for electrical by-passing.

Packed-bed electrowinning cells designed with parallel flows of current and electrolyte do not suffer from the effects of electrical by-passing, since the electrolyte is forced to pass through active regions of the bed upon entering and leaving the cathode. Mechanical by-passing is also readily prevented in this design (Paul *et al.*, 1983).

Recent improvements to the Micron solvent-distillation procedure (Muir *et al.*, 1985) for the elution of loaded carbon have enabled the eluted gold to be concentrated in a very small volume of eluate, and concentrations of gold as high as  $20 \text{ g l}^{-1}$  have been obtained. The recovery of gold in a cell containing a sufficient number of simple planar cathodes has been found to be satisfactory (Muir *et al.*, 1985).

### 15.3.4.2 Electrode reactions

The electrochemical reactions that occur at the cathode surface are almost identical to those that take place during cementation with zinc dust. The predominant reactions are therefore the reduction of oxygen, water (i.e. evolution of hydrogen), aurocyanide, and argentocyanide ions. The cyanide com-

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plexes of mercury, lead and copper will also be reduced, whereas the complexes of iron, nickel and zinc are not generally deposited. As is the case in cementation, where a large stoichiometric excess of zinc is required for a high recovery of gold, an excess of electrical current is required for the electrowinning of gold. Current efficiencies of 1 to 5% are typical, although the efficiency increases with increasing concentrations of gold. The reduction of oxygen and water consumes the excess current.

Temperature has a marked effect on the electrowinning of gold. As the conductivity of the electrolyte increases with increasing temperature, and, hence, the potential gradient across the cathode (Figure 15.19) becomes flatter, the active area of the cathode increases. Furthermore, the solubility of oxygen decreases with increasing temperature, and the current consumed by this parasitic reaction is reduced.

The only inorganic impurity that has been shown to affect the electrowinning of gold is soluble hexavalent chromium (i.e. chromate ions), which is reduced to insoluble chromic hydroxide at the cathode surface, and passivates the cathode. Chromate ions can be produced by the transpassive dissolution of stainless-steel anodes if the pH value of the electrolyte is much below 12,5. Concentrations as low as  $5 \text{ mg l}^{-1}$  can reduce the single pass efficiency for the recovery of gold to less than 10%.

The gold deposited on the cathode material is generally very fine grained and adheres poorly to the cathode. This effect is common to any electrochemical deposition process in which the cathodic process occurs under mass-transport control, and results from the very high rate of nucleation, which does not permit the existing nuclei to coalesce into a smooth deposit. It has been suggested (Paul *et al.*, 1983) that the increase in microscopic surface area of the cathode due to the presence of the gold particles could enhance the evolution of hydrogen (a reaction that is under kinetic control) at the expense of the reduction of aurocyanide ions (a reaction that is under mass transport control), which would account for the reduced single pass extractions as the cathodes become loaded with gold.

The predominant reaction at the anode is the oxidation of water to oxygen, although some cyanide may be oxidized to ammonia and carbon dioxide. If the electrowinning cells are not equipped with a ducting system to remove the gases, the odour of ammonia can become intense. The pH of the anolyte must be maintained above about 12,5 if the anodes are made of stainless steel, so that no corrosion of the alloy, and, hence, contamination of the electrolyte with chromate ions, will take place.

### 15.4 Clean-up, Calcination, and Smelting

The bullion produced in South Africa before the CIP process was introduced typically contained 88 to 90% gold and 7 to 11% silver, together with small amounts of copper, lead, zinc and iron (Adamson, 1972). The bullion is assayed for its gold content at the mine before being dispatched to the Rand Refinery for further processing. Upon receipt of this bullion by the refinery, the bullion is weighed, melted and sampled while molten. The melt

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is cast into bars and stored while the samples are assayed. When the assay and mass have been agreed with the mine, the refinery will process the bullion and the mine will eventually be paid for the gold content of the original bullion by the South African Reserve Bank.

With the advent of the CIP process, this somewhat lengthy procedure has been complicated by the presence of high concentrations of iron (5 to 8%) in the bullion produced on certain mines. The refinery has found that this bullion undergoes a degree of liquid separation while molten, and that the gold content of the two molten layers is different. The gold content of the samples taken from the melt are therefore not representative of the average gold content of the bullion, and disagreement between the Refinery and the mine concerned is inevitable.

The source of this iron contamination is the steel wool used as cathode material by those mines that recover gold from the eluates by electrowinning. Although the physical metallurgy of these metals has not been studied in any detail, it appears that the liquid separation is due to the immiscibility of liquid copper and silver with iron (Hansen, 1958), resulting in partition of the gold between layers rich in iron and those rich in copper and silver. If the iron content of the bullion is below about 3%, the extent of the separation is insignificant.

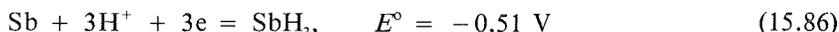
The method used for the treatment of zinc-cementation slimes is common to most mines, and involves acid treatment to dissolve the excess zinc, calcination at 600 to 800°C to oxidize the base metals, and smelting at 1200 to 1400°C with a borosilicate flux. In comparison, the treatment of steel-wool cathodes differs markedly from one plant to another, and may involve acid digestion followed by smelting of the residue, calcination followed by smelting, or even smelting without any prior pre-treatment of the cathodes (Hinds and Trautman, 1983). Digestion of the steel wool in hydrochloric acid, followed by dissolution of the residue in aqua regia, filtration to remove silver chloride, and precipitation of the metallic gold with oxalic acid or sulphur dioxide has been suggested as a possible process for smaller operators who may wish to avoid smelting (McClelland *et al.*, 1985).

### 15.4.1 Acid treatment

The slimes obtained from zinc cementation typically contain gold (30 to 40%), silver (2 to 4%), lead (5 to 15%), zinc (15 to 30%), sulphide (1 to 4%) and small amounts of copper, iron, nickel and silica. The sulphide content is due to the presence of insoluble zinc and lead sulphides. Mercury is not present to any extent in South African ores, but often attains high levels in some U.S. ores.

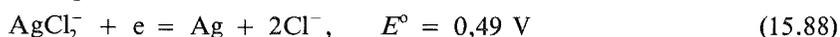
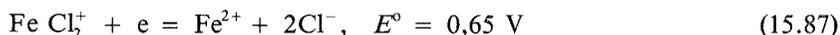
The primary objective in acid treatment (usually with sulphuric acid) is the dissolution of excess zinc. Ventilation is required to remove hydrogen sulphide, which is formed by the reaction of the acid with the lead and zinc sulphides. Most of the lead is converted to insoluble lead sulphate. If arsenic or antimony is present in the zinc slimes, the evolution of gaseous arsine,  $AsH_3$ , and stibine,  $SbH_3$ , can occur because the potentials required for the reduction of these metals

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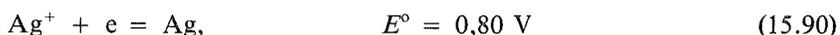
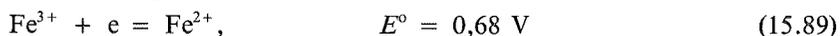


are positive with respect to the potentials at which zinc corrodes in sulphuric acid ( $-0,7$  to  $-0,8$  V). These gases are highly toxic. Some zinc sulphate may remain in the acid-treated slimes.

The steel-wool cathodes typically contain gold (60 to 70%), silver (5 to 10%), copper (5 to 10%), and iron (10 to 25%). Mercury and lead may also be present if these metals were present in the eluate. The steel wool is readily dissolved by sulphuric and hydrochloric acids, although a higher rate of reaction is achieved with hydrochloric acid. Heating to moderate temperatures (i.e. 50 to 60°C) markedly increases the rate of reaction. If the concentration of silver on the cathode is very high, some dissolution may occur in hydrochloric acid, due to the presence of chloride and ferric ions (produced by the oxidation of ferrous ions by dissolved oxygen)



The equilibrium potentials for the reduction of ferric ion and the oxidation of silver in sulphuric acid indicate that silver will not be dissolved.



### 15.4.2 Calcination

Calcination of the acid-treated residues at 600 to 800°C in an adequate supply of oxygen results in the conversion of the base metals to their oxides. The free energy per mole of oxide produced (Pankratz, 1982) is negative for all the base metals (Cu, Pb, Zn, Fe) at the temperature of calcination (Figure 15.18). The formation of silver oxide is thermodynamically favourable only at low temperatures, and becomes unfavourable at the temperatures usually employed for calcination. No thermodynamic data exist for the oxidation of gold at these temperatures, but the free-energy change is certain to be large and positive. If the cathodes are not treated with acid prior to calcination, care must be taken to ensure that an unrestricted flow of oxygen is available for the oxidation of the steel wool. Cathodes that are packed too tightly into the calcining trays will undergo oxidation only at the exposed surface. Poor oxidation of the steel wool prior to smelting is certainly the major cause of high iron values in the bullion.

Zinc sulphate is decomposed to zinc oxide and sulphur trioxide during calcination, but lead sulphate is decomposed only at temperatures approaching 1000°C. This result is to be expected from the free energies shown in Figure 15.20.

### 15.4.3 Smelting

If the calcination process has been efficiently performed, the gold and silver will be in the metallic state and all the base metals will be present as oxides

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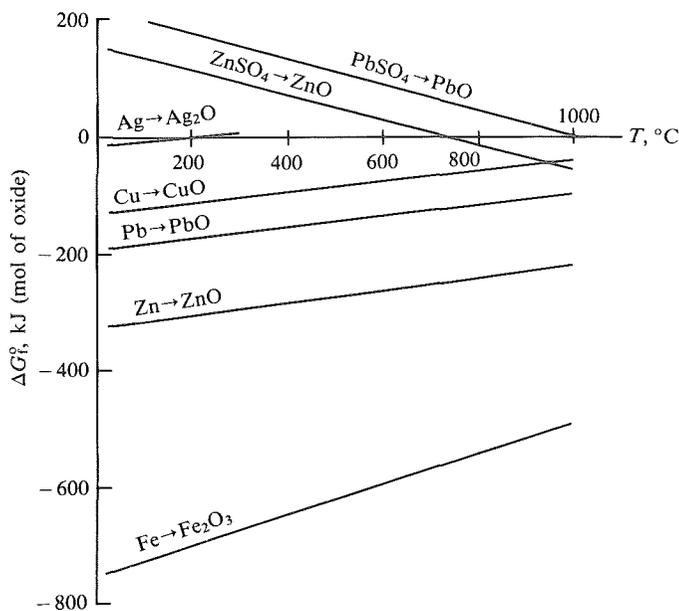
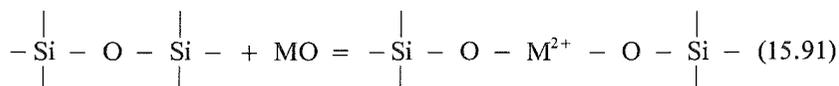


Figure 15.20. Free energy of formation of some metal oxides from the elements and by decomposition of the metal sulphates ( $P_{\text{SO}_3} = 0,001 \text{ atm}$ ).

(with the exception of lead, which is present as lead sulphate). Under these conditions, the smelting process merely requires the bullion to be melted in the presence of a suitable flux that will react with the oxides to form a stable free-flowing slag. Lead sulphate is decomposed to lead oxide and sulphur trioxide at the smelting temperature, which is usually in the range 1200 to 1400°C (the melting point of gold is 1065°C).

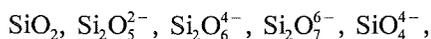
The principal component of almost all metallurgical slags is silica, i.e.  $\text{SiO}_2$  (Elliott, 1984). Silica consists of units of  $\text{SiO}_4$  in which each silicon atom is tetrahedrally surrounded by four oxygen atoms, and each oxygen atom is bonded to two silicon atoms (Turkdogan, 1983). The addition of metal oxides,  $\text{MO}$ , to molten silica results in a gradual breakdown of this structured silicate network, as represented schematically by the reaction:



The result of this reaction is the formation of a structure in which the oxygen bridge between two silicon atoms is broken. As the mole percentage of  $\text{MO}$  is increased, the number of non-bridging oxygen atoms is increased, and the network becomes progressively disordered.

A large number of structural units have been deduced from Raman spectra of silica-oxide melts of varying composition. The prominent units are:

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corresponding to an increase in the number of non-bridging oxygen atoms from 0 to 4. Attempts have been made to correlate the physical properties of the metals in terms of the formation of these structural units (Turkdogan, 1983).

The reaction between metal oxide and silica in the melt is analogous to the neutralization of an aqueous acid with oxide. A slag is therefore termed 'acidic' if it can react with 'basic' metal oxides. In terms of this loose definition, molten silica is very acidic, and remains acidic until reaction with metal oxide has broken all the Si-O-Si bonds and the only structural unit remaining is  $\text{SiO}_4^{4-}$ .

Silica alone is not a suitable flux for the smelting of gold, because of its high melting point (in excess of  $1700^\circ\text{C}$ ) and high viscosity. Both the melting point and viscosity can be reduced by the partial neutralization of silica with soda at a ratio of  $\text{Na}_2\text{O}$  to  $\text{SiO}_2$  of 50 mole per cent. However, the capacity of this slag for reaction with the base metal oxides in the calcine is then greatly reduced.

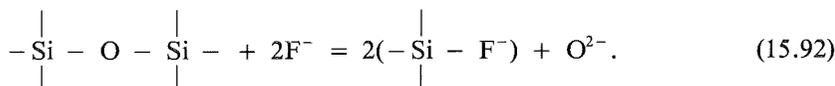
The solution to this problem is the use of a ternary slag consisting of soda, silica, and borax,  $\text{B}_2\text{O}_3$ . Borax is almost as acidic as silica, but has a melting point of  $450^\circ\text{C}$ . Much uncertainty still exists concerning the structure of  $\text{B}_2\text{O}_3$ , and reference will be made only to the critical review by Greenwood (1973). The reaction of borax with fused metal oxides results in the formation of non-bridging oxygen atoms in a fashion analogous to that of the silicates. An increase in the molar ratio of metal oxide to borax produces the following structural changes (Greenwood, 1973):



A flux consisting of equal proportions (by mass) of silica and sodium borax ( $\text{Na}_2\text{B}_4\text{O}_7$  or  $\text{NaO} \cdot 2\text{B}_2\text{O}_3$ ) is considered to be the starting point for the determination of the flux requirements for a particular smelt. The liquidus for such a mixture consisting of  $\text{Na}_2\text{O}$ - $\text{B}_2\text{O}_3$ , and  $\text{SiO}_2$  at a mass ratio of 15:35:50 is about  $800^\circ\text{C}$  (Levin *et al.*, 1964). This flux is strongly acidic, and the melt is characterized by low viscosity.

After the base metal oxides have reacted with the fluxes, the slag should be neutral or slightly acidic in order to protect the lining of the furnace (usually alumino-silicates) from attack by a basic slag. This requirement is achieved by adjustment of the total mass of flux used for the smelting process. Acid-treated, calcined zinc slimes typically require the mass of the fluxes to be 30 to 40% of the mass of the calcine to be smelted. If the slimes are not treated with acid prior to calcining, the mass of the fluxes may have to be increased to at least 50 per cent of the mass of the calcine. Owing to the increased mass of slag in these circumstances it may be advantageous to reduce the liquidus of the slag by the use of a larger amount of borax. If the viscosity of the slag is too high, calcium fluoride can be added to the flux, since the fluoride ion is a strong network breaker:

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However, the production of oxygen ions effectively increases the activity of the oxides in the slag and reduces the acidity of the slag.

Poor calcination, which does not convert the base metals completely to their oxides, usually requires the addition of an oxidant to the slag. Manganese dioxide is commonly employed if the problem is not severe:



For the treatment of steel-wool cathodes, however, where large amounts of metallic iron may be present, sodium nitrate is preferred:



because of its higher content of available oxygen. The danger associated with the use of oxidants is that silver can be readily oxidized into the slag. This problem can be avoided by acid treatment or effective calcination of the cathodes prior to smelting. The composition and mass of fluxes for any particular smelting operation must be determined experimentally.

### 15.5 Acknowledgement

This chapter is published by permission of the Council for Mineral Technology (Mintek).

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