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CHEMISTRY, PROCESSES AND PROBLEMS OF COMPLEX ORES UTILIZATION: HYDROMETALLURGICAL OPTIONS

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ABSTRACT

Since the second world war, the demands for pure elements and other metals hitherto considered rather rare, and usually found in association as complex mineral ores, have increased considerably. The utilization of these minerals as-mined has largely constituted research and technological problems. This paper has addressed the problems of complex ores utilization by considering the nature and compositions of complex ores, the multi-stage hydrometallurgical processes involved in their utilization, reagent types and consumption, energy requirements and waste disposal. The chemistry of the hydrometallurgical processes of these complex ores and the methods of separation of the constituent species has been significantly reviewed.

Key words: Hydrometallurgy, Complex ore, Leaching, Acid, Alkali, Utilization.

INTRODUCTION

Nearly all metals are derived from ores, which are concentrates of minerals situated accessibly at or near the earth's crust. Ores are complex composite materials bearing minerals of several metals. The two important exceptions perhaps are magnesium, which may also be worn from sea water, and plutonium, which is produced in atomic reactors. Ores therefore, from their own very nature are complex, the simplicity of their chemical formula notwithstanding. As the complexity of these ores increase, various technologies have been developed, effecting their laboratory analysis, industrial processes and utilizations[1-4]. Nonetheless, these utilization processes, including those still in the laboratory scales and desks, have created an avalanche of problems, in terms of capital cost with respect to engineering equipment, research and development, energy requirements, reagent consumption and waste management[5].

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Some of these ores more often than not consist of many metals, some highly entangled and others intricately locked up in interior matrices of the ore body that in almost all cases enhanced and sophisticated technologies and multi–stage processes are *sine qua non* to separation and recovery of minerals or metals of interest contained in them[6]. Some may involve pyrometallurgy, in their utilization, some requiring hydrometallurgy, while others may need both processes, and even some eventually culminate in electrometallurgical route for the recovery and refining of the valuable metals and others of secondary value[7-9].

The composition

Metals occur in the earth's crust in the following chemical forms: (i) oxides in which the metal exists in the form of oxide; these occur as primary or secondary oxides (ii) The sulphides in which the metal exists as a sulphide. Minerals of this kind are associated in families, and with iron almost always present[10]. Oxy–salts; they include the silicates, sulphates and carbonates, zircon, titanates etc. Apart from these ores, there are those found in the localities, also called "native ores", which exist in the elemental (uncombined) state. Examples are the precious metals and a little of copper. The most important groups with respect to complexity, quantity and occurrence are the oxide and sulphide ores.

Chemically, metal ores contain three categories of mineral: (i) valuable minerals of the metal being sought; they are the concentrations of the metals of economic value (ii) compounds of associated metals, which may be of secondary value, e.g. niobites, tantalites and wolframite commonly associated with cassiterite and the (iii) gangue minerals of no value, usually associated with (i) and (ii).

In order to appreciate the problems that can be envisaged in the utilization of complex ores, it may become necessary to look at the compositions of some major complex mineral ores as shown in Table 1.

Table 1: Composition of some complex ores[11,12,13]

Ore	Possible composition	Remark
Alumina	$Al_2O_3.xH_2O$	A mixture of diaspore broehmite ($Al_2O_3.H_2O$), and gibbsite, $Al_2O_3.3H_2O$). Major source of Al.
Arsenopyrite	FeAsS	Source of As and Au

Cont…

Ore	Possible composition	Remark
Carnotite	$K_2O.2UO_3.V_2O_5.3H_2O$ $K_2O.2UO_3.V_2O_5.3H_2O$	Hydrated potassiumuranyl vanadate A source of V and Ra.
Chalcopyrite	$CuFeS_2$	Major source of Cu
Cassiterite	SnO_2	Major Source of Sn
Monazite sand	(Th, La, Ce, Y, Zr, Ti, Fe,) PO_4	Major source of Th and rare earths
Pyrochlore	(Na, Ca) $(Nb, Ta)_2O_6$ (O, OH, F)	A major source of Ta and Nb
Tantaloniobates	(Fe, Mn) O. $(Nb, Ta)_2O_5$	A major source of Ta and Nb
Wolframite	(Fe, Mn) WO_4	Major source of W.
Molybdenite	Fe_2O_3. $3MoO_3$. $7H_2O$	Mixed oxides of Fe and Mo

The nature of complex ores

The dissolubility or otherwise of one or two component phases from an ore body depends on the structural complexities of the host phases, and the crystal field stabilization energies (CFSEs) of the component elements[13]. In essence, the effective utilization of such ores will have strong bearing with the internal structures, of not only the ores but also the minerals and the elemental assemblages. Geothite (α-Fe00H), for e.g., is the most frequently observed Fe bearing mineral present in Mn nodules intimately intermixed with other phases or minerals giving rise to a complex internal structure[14,15]. It is difficult, if not impossible to extract significant amount of any particular phase. However, Kumar et al.,[16] have reported that the order of leachability of Co, Cu, and Ni in H_2SO_4 from goethite show close correspondence with the CFSEs of Co(II) [92.9 KJ mol^{-1}], Cu(II) [90.4 KJ mol^{-1}], and Ni (II) [122.2 KJ mol^{-1}], suggesting that chemical nature of these elements acts as a major contributing factor on their dissolution behaviour. At low pH, the reaction of goethite with H_2SO_4 can proceed as follows:

$$\alpha\text{- }FeOOH_{(s)} + 3H^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + H_2O_{(l)} \qquad \ldots(1)$$

The imprisonment of some of the minerals/element in the crystal structure of the ores may necessitate consumption of excessive reagents, hence increasing the cost of utilization of such ores. For instance, some Au minerals are associated with the, chalcopyrite and arsenopyrite ore minerals. These cannot be treated directly by the conventional methods because of the various reasons outlined above[14,17].

Chemical characteristics

The chemical characteristics of ores influence their utilization in various ways. Different components of an ore body (oxides, sulphides, arsenides, etc.) call for different process route and reagents. One of the problems often encountered in minerals processing is non–availability of specific technologies and reaction reagents. In spite of spectacular advances in the development of extraction and floatation reagents (collector, depression, activator, etc.), the minerals processing industry is still in need of specific and selective reagents to cope with the nature of complex ores[8,14]. The donor atoms on the extraction and flotation chelating agents as well as the cations associated with the minerals in the ores play significant roles in the separation of the constituent components of an ore.

The flotation or depression of a particular component depends on the correct choice of suitable reagent for a given mineral separation. The degree of selectivity is closely related to the stability of metal/mineral complex[18-21]. An important consideration in determining the strength of a given metal–ligand interaction (or stability) is their mutual compatibility in terms of hardness and softness[3]. In this respect, metals (acceptors) and ligands (donors) are classified into hard and soft acids and bases. The metals are mostly cations and metals in zero oxidation states (called Lewis acids), while the bases are non–metal anions, neutral atoms and molecules (called Lewis base). Hard acids are small and highly charged, while hard bases are non-polarizable, and small (e.g. O and N). Furthermore, soft (donor) bases are large, and highly polrizable (e.g. S, P, Se, etc.), and so do soft acids,e.g. transition metal ions, especially in their lower oxidation states[3,22]. Generally, hard metal ions preferentially bind with hard ligands and vice versa[18,23]. One can therefore, understand why heamatite (Fe^{3+}) and pitchblende (U^{6+}), as well as Sn^{4+} and Ta^{5+} minerals bind with the chelating agent, cupferron (with O, O donor atoms) in the presence of fuel oil in a flotation cell of specified pH of 3 [24].

Most transition metals form their most stable complexes with ligands carrying O or N donor atoms. On the other hand, Pt^{2+}, $Pd^{2+,}$ Au^{+}, Cu^{+} and Hg^{2+} and other members of their group form their strongest complexes with P, S and As[3,25-27]. The hard–soft concept provides an explanation for many features of the behaviour of metal systems in mineral processing and biochemistry. For instance, most metals of lower oxidation states tend to form sulphides/sulphate ores – Fe^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Ag^{+}, Pd^{2+}, Mo^{2+}, etc., while at higher oxidation states, they form oxides/oxide minerals. By similar explanation, the sulphide minerals often prefer to bind with S–containing collectors, and oxide minerals interact with O–containing collectors in a flotation cell[3]. Therefore, in choosing chelating agents (floataids) in mineral processing systems, the chemical characteristics of the minerals have to be taken into consideration as it influences not only the solvability of the minerals but also the selectivity and collector strength of the chelating agent.

Multi – stage processes

Table 1 reveals the complexities of some of the ore minerals. This often necessitates the use of several process steps to reach the desired mineral. The processes may first involve beneficiation steps, in which the complex ore is crushed and ground, and the siliceous gangue materials reduced as much as possible[12].

The beneficiation stage may be preceded by concentration processes of flotation and magnetization to provide concentrates suitable for roasting and smelting operations. The more complex an ore is the more complex, and perhaps the greater is the number of process steps involved in the separation of the constituent minerals and the winning of the valuable metal(s). The procedures adopted to separate gangue from the valuable minerals are generally termed “ore dressing”. Ore beneficiation is also sometimes used to describe these processes, but the term when correctly applied also includes such pyro-metallurgical pre–extraction processes as calcining, sintering, pelletizing and roasting. Beneficiation, with regard to copper ores encompasses all of the methods used to process the ore to improve its physical and chemical characteristics that will make it a more desirable feed for the converter furnace or autoclave for pressure leaching. Because of the differences in structural complexities and mineral contents of ores from different deposits, beneficiation methods also vary considerably[11,28].

The beneficiation stage may be followed by roasting (Eq.2) and agglomeration,

$$MS + O_2 \longrightarrow MO + SO_2 \qquad \ldots(2)$$

$M = Zn, Cu, Ni$, etc.;

Then leaching by a leachant and precipitation by a precipitant (HL) or hydrolysis by change of pH.

$$M^{n+} + nHL \longrightarrow ML_n + nH^+ \qquad \ldots(3)$$

or $M^{n+} + 3OH^- \longrightarrow M(OH)_3$

The choice of any extraction route will largely depend on the cost per tonne of metal produced, the type of ore, availability and cost of fuel, and the quantity and quality of products of such a process[27]. Sometimes the utilization of a particular ore may involve the three processes outlined in the extraction of Al from bauxite. Others may involve only two process steps, such as the production of electrolytically refined Ni or Cu from molten matte. Some processes which focus on two major steps include the recovery of copper and iron from chalcopyrite by oxidative leaching[28]. It is then followed by solvent extraction using an organic extractant, to bring about impurities removal. This may be followed by a third step, the electrolytic process.

Hydrometallurgy

While pyro-metallurgy is most suitable for treating high-grade ores, hydrometallurgy is more suitable for low grade complex oxide ores and sulphidic concentrates. Hydrometallurgy encompasses all aqueous processes involved in treating ores, minerals, concentrates, etc. to recover metals or their values. They may include leaching, solvent extraction, ion exchange, precipitation, electro-winning and electro-refining.

This method of treating complex ores involves the recovery of metals by the use of aqueous medium to dissolve one or more metal values from ore concentrates; and it offers great potentials for reduction of air pollution and solid residue generation[29]. Metal is recovered from solution by electrolysis or by precipitation either in the elemental form (cementation) or as a compound suitable for pyro-metallurgical treatment[29]. Precipitation results in the preferential selection of a metal ion or group of metal ions being thrown out of solution in a solid form[30,31], while isolation or concentration techniques result in the preferential selection of a metal ion or group of metal ions in a suitable solvent (SX or IX)[32].

These processes have permitted the economic extraction of metals, e.g. Cu, from very low grade ores and old mine dumps, and have contributed immensely to the recent increase in the relative importance of hydrometallurgical operations[33-36]. Treatment of complex ores may necessitate the simultaneous use of high temperatures and pressures to bring about leaching (e.g. Al), precipitation and even production of solid metals (e.g. Au). These are very costly processes and often constituting design problems; such as in the use of autoclaves, high pressure pumping machines and materials of construction. Pressure hydrometallurgy, for example, gives rise to corrosive and erosive conditions, and consequently the proper selection of materials of construction is an important factor in the design[42,43]. Costly corrosion resistant materials such as stainless steel and polyplastics find wide applications in this respect.

The oxides

Hydrometallurgy has become a useful tool in the recovery of many metals from complex oxide ores, such as aluminum, uranium and niobium/tantalum.

Aluminum ores

The only ore from which aluminium (Al) is industrially and profitably extracted is bauxite ($Al_2O_3.nH_2O$). Bauxite is a mixture of aluminum hydrated oxides, with oxides of Si, Ti, and Fe as the main impurities[39]. The problems associated with bauxite utilization lies on the refractory nature of the ore and the high affinity aluminum has for oxygen. This makes the pyrometallurgical production of Al from bauxite highly expensive and energy intensive, in terms of furnace wears and high temperature requirements. This is unlike the extraction of most metals by smelting their oxides with cheap reducing agent, carbon and the resultant crude metal refined by the oxidizing action of air.

Aluminum has higher affinity for oxygen (O_2) than carbon (C), and cannot be economically separated from O_2, by the usual pyrometallurgical methods. Aluminum oxide cannot melt below 2000^{o}C, and is not reduced by heating with H_2; and heating strongly with carbon only produces the carbide, Al_4C_3. A hydrometallurgical process of leaching has been invented that circumvents these problems. It is called the 'Bayer's Process', named after the inventor, Karl Josef Bayer, an Austrian Chemist. The process produces a high purity concentrate called alumina, which is subsequently used in a fused salt electrolysis to produce pure Al[39].

The Bayer process involves the extraction of aluminum by leaching finely crushed bauxite with strong caustic soda (30%) solution at high temperature (120-250^{o}C) and pressure (5-30 atm) in large steam-agitated pressure vessels (or autoclaves). It is purified by means of precipitation of the hydroxides.

The process conditions of the leaching processes are dictated by the type of minerals present in the ore. The minerals in a natural bauxite may be trihydrate, $Al_2O_3.3H_2O$ (or $Al(OH)_3$, called gibbsite), or the monohydrate, $Al_2O_3.H_2O$ (or simply AlO(OH)), which consists of diaspore and boehmite[39,12]. Operating within a certain temperature range (120 – 250^{o}C) will be necessitated by the proportions of the monohydrate and the trihydrate minerals present in the ore. While the less thermodynamically stable trihydrate dissolves more readily at lower temperatures, the monohydrates will require higher temperatures (up to 500^{o}C) or stronger caustic soda or both[10]. Raising the temperature also increases the rate at which Si goes into solution and operating at higher temperatures, however, are inadvisable because of the possible deposition of calcium aluminum titanate on the heating reactor surfaces, which are difficult to dissolve.

Aluminum oxides dissolve in the presence of NaOH to form sodium aluminate.

$$Al_2O_{3(s)} + 2\ NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O \qquad \ldots(4)$$

The associated Fe, Si, and Ti oxide impurities remain as residues.

Iron is precipitated as an insoluble ferric hydroxide

$$Fe^{3+}{}_{(aq)} + 3\ OH^{-}{}_{(aq)} \longrightarrow Fe(OH)_3 \qquad \ldots(5)$$

and Ti as hydrated titanium oxide,

$$TiO^{2+}{}_{(aq)} + 2\ H_2O \longrightarrow TiO(OH)_2 + 2H^{+}{}_{(aq)} \qquad \ldots(6)$$

while Si dissolves in the alkaline solution as Sodium Silicate

$$SiO_2{}^{2+}{}_{(s)} + 2\ NaOH_{(aq)} \longrightarrow Na_2SiO_{3(aq)} + H_2O \qquad \ldots(7)$$

which subsequently recombines with sodium and aluminate ions present in solution to precipitate as an insoluble sodium aluminum silicate.

$$2\ NaSiO_{3(aq)} + Na^{+}{}_{(aq)} + Al\ (OH)_4{}^{-}{}_{(aq)} \longrightarrow NaAlSi_2O_{6(s)} + 4\ NaOH_{(aq)} \qquad \ldots(8)$$

This forms part of the red mud or sludge commonly associated with Bayer's process[45,48].

The extracted aluminum is pumped into the precipitation tanks to cool, whereby Al hydroxide precipitates as follows:

$$NaAlO_{2(aq)} + 2\ H_2O \longrightarrow Al\ (OH)_{3(s)} + NaOH_{(aq)} \qquad \ldots(9)$$

$Al\ (OH)_3$ seeds accelerate the nucleation and growth of the precipitated.

Finally, the precipitate is settled, filtered, and strongly heated to about 1100-1350°C to yield 99.95% pure alumina powder for electrolytic extraction of aluminum metal[46].

$$2\ Al\ (OH)_3 \longrightarrow Al_2O_{3(s)} + 3H_2O \qquad \ldots(10)$$

Disposal of the Al residue is a major environmental problem associated with Al extraction and refining[49-51]. Its disposal and/or re-use adds to the cost of producing aluminum.

Tantalum and niobium ores

Tantalum and Niobium have very strong similar chemical and thermodynamic properties, and as such, occur together in many minerals, and are very difficult to separate. The most important minerals occur as complex oxides, namely pyrochlore, a mixed oxide of tantalum-niobium, sodium and calcium, $[(Na, Ca) (Nb, Ta)_2O_6 (O, OH, F)]$ and tantaloniobites, a mixed oxide of tantalum-niobium, iron and manganese, all of which share the general formula $(Fe, Mn) O. (Nb, Ta)_2O_5$, which forms an isomorphous series in which Ta and Nb replace each other in all proportions[52]. The minerals in which Nb predominates are called columbites or niobites (Nb_2O_5), while the term tantalite is used for those containing over 50% Ta_2O_5, depending on the ore and location[44,53]. Ta_2O_5 and Nb_2O_5 occur in Nigeria in association with cassiterite; and between 1933 and 1954, she ranked amongst the first three greatest producers of columbite[40]. Because of their great affinity for one another, their utilization has been seriously hampered.

Beneficiations to produce Nb_2O_5 and Ta_2O_5 concentrates have been tedious and expensive; often requiring leaching at high temperatures (150°C) and pressures (1000 Kpa) and for long duration. These refractory oxides are not attacked by mineral acids at ordinary temperatures, except as a mixture of HCl and HNO_3 or HF to form anionic and flouro- complexes of these metals: $NbOF_5^{2-,}$ $NbOF_6{}^{2-}$, NbF_6^{2-}, TaF_7^{2-} and TaF_8^{3-}, etc[3,41,42]. Interestingly, the use of HCl and other chlorinating agents has been successfully applied at a comparatively low temperatures and pressures to recover Ta and Nb from their ores[43-46]. In nitric acid media, substantial amounts of Ta are said to be recovered using highly concentrate solutions of HNO_3 within 120 minutes[47].

$$3\,(Fe, Mn)\,O.\,(Ta, Nb)_2O_5 + HCl \longrightarrow TaCl_6^-, NbCl_6^-$$

$$\text{or } (Ta, Nb)\,Cl_6^- + FeCl_3 \qquad \ldots(11)$$

In the case of columbite containing tin, SnO_2 dissolves as haloacids to give hexahalostannates:

$$SnO_2 + 6\,HCl \longrightarrow H_2Sn\,(Cl)_6 + 2\,H_2O \qquad \ldots(12)$$

Alkali fusion also offers another route for the recovery of Ta and Nb oxides, followed by dilute acid leaching[37,48,49]. The reactions of niobium–tantalum minerals with alkali solutions are as follows[50,51].

$$3\,(Fe, Mn)\,O.\,(Ta, Nb)_2O_5 + 8\,KOH + (n\text{-}4)\,H_2O \longrightarrow$$

$$K_8\,[(Ta, Nb)_6O_{19}.nH_2O)] + 3\,(Fe, Mn)\,O \qquad \ldots(13)$$

K_8 [(Ta, Nb)$_6$O$_{19}$.nH$_2$O)] $\longrightarrow$ 6 K (Ta, Nb) O$_3$ + 2 KOH + (n-1) H$_2$O …(14)

Reaction (30) may be expressed as follows:

$[(Ta,Nb)_6\ O_{19}.nH_2O)]^{8-} \longrightarrow (Ta,Nb)_6O_{19})^{8-} + nH_2O$ …(31)

$[(Ta,Nb)_6O_{19})]^{8-} + H_2O \longrightarrow 6(Ta,Nb)O_3^{-} + 2\ OH^{-}$ …(15)

The presence of the soluble and insoluble forms of niobium and tantalum will depend on the reaction conditions and the type of ore being processed.

The Sulphides

Sulphide ores, though appearing simple with respect to chemical formulae, are the most complex of all mineral ores. This is so, for example, chalcopyrite, a sulphide of Cu and Fe, contains almost all the elements in the periodic table that form sulphides (eg, Pb, Hg, As, Te, Se, Zn, Cd, Ni, Co, etc.). This makes the utilization of sulphide ores rather problematic. It may involve a series, but cumbersome processes that may culminate in electrolysis of the impure aqueous concentrate.

The most extensively studied sulphides are those of Pb, Zn, Cu, Co. Ni and Ag. A typical sulphide of interest is the abundant copper bearing mineral, the chalcopyrite, $CuFeS_2$, which can readily be enriched by floatation processes to yield a concentrate which contains 30% Cu, 30% Fe and 30% S, the balance being Ni, Co, Ag, Zn and gangue minerals. Hydrometallurgical processes have been useful in the treatment of such ores, and seem exclusive reserve of complex oxides and sulphidic ores. In several process systems, sulphur in the ore is transformed directly to elemental sulphur in the presence of an oxidizing agent, or the SO_2 produced is converted to H_2SO_4 to be used locally for leaching processes[8,67,68].

$3\ ZnS_{(s)} + 8\ HNO_{3(aq)} \longrightarrow 3\ Zn^{2+} + 6\ NO_3^{-}{}_{(aq)} + 3\ S^o + 2\ NO_{(g)} + 4\ H_2O$ ...(16)

$2\ CuFeS_{2(s)} + 2\ H_2SO_4 + 2\frac{1}{2}\ O_{2(g)} \longrightarrow 2\ CuSO_{4(aq)} + 2\ FeOOH + 4\ S^o + H_2O$ ...(17)

The technique has been utilized in Duval`s CLEAR and Cyprus processes[69-71]. The processes require leaching $CuFeS_2$ concentrate with a solution of ferric salt and cupric chloride (as oxidizing agents): This chloride leaching method has recently been revisited by Lidicoat, et al.[28] who demonstrated that the method could become one of the most important means of exploiting mixed and polymetallic ores at relatively minimum cost.

$CuFeS_2 + 3\ FeCl_3 \longrightarrow CuCl_2 + 4\ FeCl_2 + 2\ S^o$ …(18)

$CuFeS_2 + 3\ CuCl_2 \longrightarrow 4\ CuCl + FeCl_2 + 2\ S^o$ …(19)

Part of Cu is recovered by electrolysis which also regenerates the leaching reagent (CLEAR = Copper, Leach, Electrolysis and Regeneration). Oxygen is used as the oxidizing agent under pressure to solubilize the remaining $CuFeS_2$ in a second step leaching process:

$$2\ CuFeS_{2(s)} + H_2SO_{4(aq)} + 4\ O_2 \rightarrow 2\ CuSO_{4(aq)} + Fe_2O_{3(s)} + H_2O + 3\ S^o_{(s)} \qquad \ldots(20)$$

Iron is usually precipitated as $Fe(OH)_3$, FeOOH or Fe_2O_3 depending on the conditions of temperature and oxygen potential in these oxidative leaching of pyrites.

The processing of Pb–Zn-Cu complex sulphide ore involves both the pyrometallurgical and hydrometallurgical routes. A lot of steps are involved. The pyrometallurgical methods are non-selective and energy intensive, but the hydrometallurgical methods are based on the selectivity of the reagents upon the selected concentrates. One interesting method is be the selective separation of lead, from complex Pb–Zn-Cu sulphide by mobilizing some associated metals into soluble sulphate forms[73] as shown by the following equations:

$$MS + 2\ H^+_{(aq)} \longrightarrow M^{2+}_{(aq)} + H_2S_{(g)} \qquad \ldots(21)$$

where M = Fe, Zn, and Cu

and

$$PbS + 2\ H^+_{(aq)} \longrightarrow PbSO_{4(s)} + H_2S_{(s)} \qquad \ldots(22)$$

In the natural ore system, it is difficult to achieve the ideal condition which would make separation practicable. But three processing stages could be utilized to achieve this; the reducing phase, oxidation phase and $PbSO_4$ separation stage.

For the reduction reaction, the ore would be reacted with H_2SO_4, to extract all soluble Fe and initiate responsible displacement reactions at the appropriate pH value. It could be observed that Fe^{2+} in the presence of H_2SO_4 has a limited solubility. If the quantity of soluble Fe^{2+} is not controlled, the following reaction may occur

$$6\ FeSO_4 + x\ H_2O + 3\ O_2 \longrightarrow 3\ Fe_2O_3.2\ SO_3.x\ H_2O \qquad \ldots(23)$$

To maximize Fe^{2+} solubility under this condition, the acid is added rapidly under non-aerative condition so as to impose temporary reducing condition upon the system. The presence of galena, however, creates a problem by causing the reaction to cease due to the formation of an insoluble film of $PbSO_4$ on the ore particles.

$$PbS + H_2SO_{4(aq)} \longrightarrow PbSO_{4(s)} + H_2S_{(g)} \qquad \ldots(24)$$

At this stage liquid-solid separation are made and a new equilibrium is established. All the sulphide minerals in the system are exposed to an exchange reaction based upon the solubility product principle. The sulphide mineral surfaces are inhibited by a film of covellite (CuS). This is done by adding a pre-established amount of Cu^{2+} in soluble form to the system. Cu^{2+} can be derived from copper salts which are readily available for the reaction:

$$ZnS + Cu^{2+} \longrightarrow CuS + Zn^{2+}_{(aq)} \qquad \ldots(25)$$

In these hydrometallurgical processes the constituent components of the mixed sulphide ore are separated and some forced into solution.

Reagents

One of the major problems associated with hydrometallurgical processing of complex ores is the high cost of reagents. These may include the cost of obtaining suitable frothers, collectors, depressants, activators, etc. for flotation processes, and leaching agents like NH_4Cl, $FeCl_3$, $FeSO_4$, HCl, H_2SO_4, $(NH_4)_2CO_3$, etc. Because of the complex nature of some of these ores, specialized costly reagents may be required.

The use of acid or alkaline leaching depends on the composition of the ore and cost of the reagents. Precipitation of U compounds from acid solutions is more costly than from basic solution, even though the former is mostly used. The use of costly reagents in the recovery of metals from ores or synthetic metal compounds by solvent extraction techniques has been recorded[36,74] especially with chlorinated and fluorinated beta-diketones and substituted acyl pyrazolones.

The cost of obtaining polymeric resins for IX processes, and specialized β-ketone extractants for SX, both of which are separation and concentration processes, appear to impose limitations to our ability to utilize these complex ores by hydrometallurgical options

Waste problems

One of the results of the utilization of complex ores is the generation of barren solutions and solid wastes. The indispensability of these wastes have in some cases constituted environmental problems as a result of failures of previous attempts – recurring spills and failures of conventional tailings disposal pond dams etc.(Robinsky, 1999). Because of the complex nature of some of these ores, their utilization often involves some complex treatments requiring specific extraction routes and reagent types. In the case of separating and extracting minerals of value from the gangue, large amounts of mineral wastes, residues, tailings and slags are produced, which accumulate over the years.

For instance, the hydrometallurgical treatment of bauxite Al ore, the produces large tonnages of red mud, which is composed mainly of Fe_2O_3, TiO_2, SiO_2, some hydrated sodium aluminium silicates, etc. About 400 million tonnes of this residue is produced annually world-wide[76,77]. Disposal problems are bound to arise, particularly in places where the technology of converting sulphur in suphidic ores to the elemental form or other suitable sulphur compounds are not available. Due to various transportation, technological and economic reasons these varieties of wastes are found stock-pilled around metallurgical sites.

Cyanides are poisonous compounds. But in the hydrometallurgy of Au, Ag, etc, which may include cyanidation process, it is often the practice to bleed or eliminate part of the cyanide from time to time to avoid the accumulation of impurities which may interfere with the leaching step[18]. The disposal of this bleed solution has been a problem and will continue to be so until when technologies have been developed to convert HCN and its compounds to harmless species.

Although the extraction of metals from complex ore from aqueous solution are never complete[32,2], the processing of complex ores are advancing to a cleaner production with over 90% conversion[43-46]. The problem of waste disposal has serious adverse effect on the environmental condition of the terrain; heavy metals penetrate soils and poison underwaters, etc.

Sulphuric acid is the cheapest and the most easily available, and therefore, the most commonly used[78,79]. Pollution problems associated with the treatment of certain ores with H_2SO_4 seem to limit its use despite the advantages. They include:

(i) The formation of ferrous sulphates when the feed material contain appreciable amounts of iron. This creates disposal problem because it is difficult to decompose and costly to modify.

(ii) The presence of radium (Ra), a uranium decay product, in the residue when U is treated with H_2SO_4, and which may disintegrate into the radioactive gas, radon (Ra), diffuse into the environment, scatter as dust particles by wind, and the leaching of the resultant residue dumps by water solution constitute environmental problems.

Ra-226, a product of the radioactive decay of U-238 occurs in the lattice of minerals formed by the latter, and might be expected to dissolve with U during H_2SO_4 leaching[1]. The fact that this does not happen implies that Ra (90%) precipitates from leach solution in the form of the insoluble, $RaSO_4$ salt.

To overcome the above problems, other alternative leaching systems capable of achieving simultaneous extraction of U and Ra are being developed or applied. Chloride and nitrate systems appear to be more attractive alternatives to H_2SO_4 in this regard, as they form mostly solube salts and complexes of various metals[55,57].

By solubilizing Ra along with U, it would be possible to isolate Ra in a concentrate of small mass that could consequently be disposed in a more controlled manner[58-60].

CONCLUSION

Hydrometallurgy has become one of the best methods presently employed in the treatment of complex ores. Acids and alkalis have proved to be very efficient in the dissolubility of one or more component phases of the ore bodies. The use of mixed leaching reagents, high temperatures and pressures, and microbial organisms, have proved to be effective in metal values recovery from complex ore bodies. With hydrometallurgy, treatment of waste solid residues has become easier to handle. Concentration and impurity separation processes of precipitation, solvent extraction and ion exchange generate pure metal values from which metal values of high purity are produced by other appropriate methods such as electrowinning.

REFERENCES

1. F. Habashi, Recent Advances in Pressure Hydrometallurgy, In: International Conf. on Advances in Chemical Metallurgy., No. **8**, pp. 1-35, Bombay, India (1979a).
2. M. O. C. Ogwuegbu and E. Orji, Liquid-liquid Extraction Separation of Uranium (VI) and Nickel (II) by a Substituted Oxo-pyrazole, Minerals Engineering, Vol. **10(11)**, (1997) pp. 1269-1278.
3. M. O. C. Ogwuegbu and F. Chileshe, Coordination Chemistry in Mineral Processing, Min. Proc. and Extr. Metall. Rev., Vol. **21**, 497-52 (2000).
4. G. O. Onyedika, M. O. C. Ogwuegbu, J. Hwang and A. Ayuk, P. Zhiwei, L. Bowen and E. N. O. Ejike, M. Andriese, Mineralogical Characterization of Kuru Cassiterite Ore by SEM-EDS, XRD and ICP Techniques, JMMCE (IN PRESS) (2011).
5. Rybakov et al., Microwave field distribution inside an oversized cavity: Comparison of calculation within the ray tracing method with exact solution. 7th International Conference on Microwave and High Frequency Heating, Valencia, Spain (1999).

6. D. S. R. Murthy, Microbially Enhanced Thioura Leaching of Gold and Silver from Lead-Zinc Sulphide Flotation Tailings, Hydromet., **25**, 51-60 (1990).
7. L. Huai-zhong, C. Li-yuan and Q. Wen-qiug, Galena – Pyrolusite Co- extraction Insodium Chloride Solution and its Electrochemical Analysis, Trans. Nonferrous. Met. Soc. China, **20**, 897-902 (2010).
8. A. O. Adebayo, K. O. Ipinmorati and O. O. Ajayi, Leaching of Sphalerite with Hydrogen Peroxide and Nitric Acid Solution, J. Min. Metall. Charact. Engr., **5(2)**, 167-177 (2006).
9. S. F. Wang, Z. Fang and Y. F. Tai, Application of Thermo-Electrochemistry to Simultaneous Leaching of Sphalerite and MnO_2, J. Therm. Anal. Calorim., **85(3)**, 741-743 (2006).
10. J. D. Gilchrist, Extraction Metallurgy, 2nd Edition, Pergmon Press, Oxford, (1980) pp. 355.
11. H. H. Read, Rutley`s Elements of Mineralogy, 26th Edition, Thomas Murby and Co., London (1972).
12. C. S. Hurlbut, Minerals and How to Study Them, 3rd Edition, John Wiley and Sons, Inc., New York, 120 – 260 (1949).
13. B. A. Wills, Mineral Processing Technology: An introduction to the Practical Aspects of Ore Treatment an Mineral Recovery, 2nd Edition, Pergamon Press, Oxford, 1-4 (1981).
14. J. A. Vezina, Acid Leaching of a Pentlandite–Chalcopyrite–Pyrrhotite Concentrate, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Techn. Bull., **129** (1970).
15. J. W. Murray, Iron oxides, In: Burns P.G. (Eds), Marine Minerals, Mineralogical Soc. of America, Washinghton D.C., 6:47-97* (1979).
16. A. Thijs, G. D. Roy, E. F. Vansant and G. P. Glasby, T. Thijssen, Mossbauer Effect Studies of Fe in Mn Nodules and Associated Marine Sediments in Five Areas in the Equatorial and S.W. Pacific, Geochem. J., **15**, 25-37 (1981).
17. R. Kumar, R. K. Ray and A. K. Biwas, Hydrometallurgy **25**, 61-63 (1990).
18. Y. J. Hsu, T. Tran, Selective Removal of Gold from Copper-Gold Cyanide Liquors by Cementation Using Zinc, Minerals Engineering, Vol. **9**, No. 1, (1996) pp. 1-3.

19. T. L. Ho, Chem. Review, 75, **(1)** (1975)

20. D. R. Nagaraj, The Chemistry and Applications of Chelating or Complexing Agents in Minerals Separations : In Reagents in Mineral Processing, Mercel Dekker (1989) p. 267.

21. A. C. Achusim-Udenko, G. Onyedika, M. O. C. Ogwuegbu and A. Ayuk, Flotation Recovery of Baritefrom Ore Using Palm Bunch Based Collector, Int. J. Chem. Sci., **9(3**), 1518-1524 (2011).

22. I. Flening, Frontier Orbitals and Organic Chemical Reactions, Wiley, London (1976).

23. J. E. Hulecy, E. A. Keiter and R. L. Keiter, Inorganic Chemistry: Principles and Reactivity, 4th Edition, Harper Collins Publishers, New York, (1993) pp. 387-572.

24. N. G. Yamada and S. Miki, Bull. Chem. Soc. Jap., **36**, 680 (1963).

25. S. N. Podder, K. Dey and N. G. Poddler, Indian J. Chem., **8**, 364-367 (1970).

26. B. Mason, C. B. Moore, Principles of Geochemitry, 4th Ed., John Wiley and N. Y. Sons (1982).

27. M. O. C. Ogwuegbu, Applications of Precipitation Technigues in Mineral Processing: Processes and Chemistry, Int. Conf. on Mining Which Way, University of Zambia, Lusaka, 22-24th June, 1998 (1999).

28. J. Lidicoat, D. Dreisinger, Chloride Leaching of Chalcopyrite, Hydrometallurgy, **89**, 323-331 (2007).

29. D. S. Miroslav, M. Branislav and Z. Dragana, Kinetics of Chalcopyrite Leaching by Sodium Nitrate in Sulphuric Acid, Hydrometallurgy, **95**, 273-279 (2008).

30. F. Habashi, Chemical Metallurgy, Chemistry, Vol. **45**, (1972) pp. 6-10.

31. J. J. More, Chemical Metallurgy, Butterworths, London, (1981) pp. 260-268.

32. M. O. C. Ogwuegbu and N. C. Oforka, Solvent Extraction Separation Studies of Iron (III), Cobalt (II), Nickel (II) and Copper (II) from Aqueous Solution with L-Phenyl-3-Methyl-4-(P-Nitrobenzoyl)-5-Pyrazole, Hydrometallurgy, **34**, 359-367 (1994).

33. N. N. Saxena and N. R. Mandre, Mixed Control of Copper Dissolution for Copper Ore Using Ferric Chloride, Hydrometallurgy, **28**, 111-117 (1992).

34. T. Havlik, M. Skrobian, P. Balez and R. Kammel, Leaching of Chalcopyrite Concentrate with Ferric Chloride, Int. J. Mineral Processing, **43**, 61-72 (1995).

35. T. Havlik, M. Laubertova, A. Miskufova and J. Kondas, F. Vranka, Extraction of Copper, Zinc, Nickel, and Cobalt in Acid Oxidative Leaching of Chalcopyrite at the Presence of Deep –Sea Manganese Nodules as Oxidant, Hydrometallurgy, **77**, 51-59 (2005).

36. Y. L. Mikhlin, Y. V. Tomashevich, I. P. Asaov and A. V. Okotrub, V. A. Varnek, and D. V. Vyalikh, Spectroscopic and Electrochemical Characterization of the Surface Layers of Chalcopyrite Reacted in Acidic Solutions, Applied Surface Sciences, **225**, 395-409 (2004).

37. O. M. El – Hussaini, M. A. Mahdy, Sulphuric Acid Leaching of Kab Amiri Niobium – Tantalum Bearing Minerals, Central Eastern Desert, Egypt, Hydrometallurgy., **64**, 219 -229 (2002).

38. F. Habashi, Recent Advances in Hydrometallurgy, 13th lnternational Mineral Processing Congr., Warsaw (1979b) pp. 609-633.

39. J. W. Evan, Electricity in the Production of Metals, from Aluminium to Zinc, Met. Metall. Trans., **26B**, 189-208 (1995).

40. O. Ofor, The Mineral Wealth of Nigeria, Oliverson Industrial Publishing House, Owerri (1994) pp. 10.

41. D. E. Davey, R. W. Attrall, T. J. Cardwell and R. J. Mayee, The Mechanism of Extraction of Niobium (V) from Hydrochloric Acid by (3,5,5-Trimethylhexy) Ammonium Chloride Dissolved in Chloroform etc., J. Inorganic Nuclear Chem., **41**, 1199-1203 (1979).

42. L. Maya, R. J. Hydzik and J. A. Haas, Niobium (V) Extraction by Butyl Laurylphosphoric Acid from Nitric Acid, J. Inorg. Nucl. Chem., 1193-1195 (1979).

43. E. A. Brocchi, F. J. Moura, Chlorination Methods Applied to Recover Refractory Metals from Tin Slags, Mineral Engineering, **21**, (2008) pp. 150-156.

44. T. Li, Experimental Studies of the Solubility of Cassiterite and the Extraction of Tin from Granitic Melts, Chin. J. Geochem., **Vol. 8(1)**, 84-96 (1989).

45. C. K. Gupta, A. K. Suri, Extractive Metallurgy of Niobium, CRC Press, London, (1994a) p. 98.

46. C. K. Gupta, A. K. Suri, Extractive Metallurgy of Niobium, CRC Press, London, 125 (1994b).

47. A. A. Baba, F. F. Adekola, O. I. Dele-Ige and R. B. Bale, Investigation of Dissolution of a Nigerian Tantalite Ore in Nitric Acid, J. Minerals and Mater. Charact. Eng., **7(1)**, 83-95 (2007).

48. R. A. Foos, Recovery of Columbium Values, U.S. Patent 2953453 (1960).

49. P. B. Cardon, Process for Recovering Niobium and Tantalum from Ores and Ore Concentrates Containing Same. U.S. Patent 3058825 (1962).

50. K. A. Foo and B.W. Lightfoot, Operation of a 4th Matte Fuming Pilot Plant, Proc. Pryomet. 87. Inst. Min. Met., London, 389 (1987).

51. A. N. Zelikman and M. A. Orekhov, Decomposition of Tantalum Concentrates by Sodium and Potassium Hydroxides at Increased Temperatures and Pressures, Izvestia Akademii Nauk SSSR Metally **6** (1965) pp. 38-45 (in Russia).

52. A. N. Zelikman and M. A. Orekhov, Study on the Dissolution Behaviour of $K_8Nb_6O_{19}.16H_2O$ in KOH Solution Under High Temperature. Izvestiya Akademii Nauk SSSR, Neproganicheskie Materialy, **8** (1972) pp. 1451-1454 (in Russia).

53. S. Guy, G. J. Lawson, P. Broadbert and J. D. J. Jackson, Cupric Chloride Leaching of a Complex Cu-Zn-Pb Ores, Hydrometallurgy., **10**, 243-255 (1983).

54. F. Habashi, Environment Issues in the Metallurgical Industry; Progress and Problems, Environ Issues and Waste Management in Energy and Minerals Production, **Vol. 2**, (1992) pp. 1143.

55. C. Hanahan, D. McConchie, J. Pohl, R. Creelman, M. Clarke and C. Stocksiek, Chemistry of Seawater Neutralization of Bauxite Refinery Residues, Environ. Engg. Scis., **21(2)**, 125-238 (2007).

56. M. O. C. Ogwuegbu, Applications of HCI and HNO_3 in Aqueous Chemistry of Metals: A Review, Nigeria J. Sci. Technol., **1(1)**, 2-11 (1998).

57. J. Vinals, C. Nunez and J. Carrasco, Leaching of Au, Ag, and Pb from Plumbojarosite-Containing Haematite Tailing in HCI-$CaCI_2$ Medium, Hydromet., **26**, 179-199 (1991).

58. F. Habashi, Environmental Issues - Prospects and Problems. In: Environmental and Waste Management in Energy and Minerals, Singhal et al., (Eds.) Balkena, Rotterdam, (1991) pp. 1143-1153.

59. F. Habashi, Environmental issues in the metallurgical industry; Progress and Problems, Environ. Issues and Waste Management in Energy and Minerals Production, Vol. 2 (1992).

60. C. He and H.Z. Liu, Treatment of fluorine–containing waste gas from hydrometallurgical of tantalum and niobium, Nonferrous Metals, 4, 141-142, (1998).

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