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 utilizations1-4. 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 management5.

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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. 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. 

**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. 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**

<table>
<thead>
<tr>
<th>Ore</th>
<th>Possible composition</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>Al₂O₃.xH₂O</td>
<td>A mixture of diaspore broehmite (Al₂O₃.H₂O) and gibbsite, Al₂O₃.3H₂O. Major source of Al.</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>FeAsS</td>
<td>Source of As and Au</td>
</tr>
</tbody>
</table>

Cont...
<table>
<thead>
<tr>
<th>Ore</th>
<th>Possible composition</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carnotite</td>
<td>K₂O₂UO₅.V₂O₅.3H₂O</td>
<td>Hydrated potassiumuranyl vanadate</td>
</tr>
<tr>
<td></td>
<td>K₂O₂UO₅.V₂O₅.3H₂O</td>
<td>A source of V and Ra.</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>Major source of Cu</td>
</tr>
<tr>
<td>Cassiterite</td>
<td>SnO₂</td>
<td>Major Source of Sn</td>
</tr>
<tr>
<td>Monazite sand</td>
<td>(Th, La, Ce, Y, Zr, Ti, Fe,) PO₄</td>
<td>Major source of Th and rare earths</td>
</tr>
<tr>
<td>Pyrochlore</td>
<td>(Na, Ca) (Nb, Ta)₂O₆(O, OH, F)</td>
<td>A major source of Ta and Nb</td>
</tr>
<tr>
<td>Tantaloniobates</td>
<td>(Fe, Mn) O. (Nb, Ta)₂O₅</td>
<td>A major source of Ta and Nb</td>
</tr>
<tr>
<td>Wolframite</td>
<td>(Fe, Mn) WO₄</td>
<td>Major source of W.</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>Fe₂O₃. 3MoO₃. 7H₂O</td>
<td>Mixed oxides of Fe and Mo</td>
</tr>
</tbody>
</table>

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. 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-FeOOH), for example, 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. It is difficult, if not impossible to extract significant amount of any particular phase. However, Kumar et al. have reported that the order of leachability of Co, Cu, and Ni in H₂SO₄ 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 H₂SO₄ can proceed as follows:

\[
\alpha-\text{FeOOH}_{(s)} + 3\text{H}^+_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + \text{H}_2\text{O}_{(l)} \quad \ldots(1)
\]

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.
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. 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. 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. 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. Generally, hard metal ions preferentially bind with hard ligands and vice versa. 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.

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. 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 possible12.

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 considerably11,28.

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

$$\text{MS} + \text{O}_2 \rightarrow \text{MO} + \text{SO}_2 \quad \ldots(2)$$

$$M = \text{Zn, Cu, Ni, etc.};$$

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

$$\text{M}^{n+} + n\text{HL} \rightarrow \text{ML}_n + n\text{H}^+ \quad \ldots(3)$$

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

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. 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 chalcopryite by oxidative leaching. 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. 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. Precipitation results in the preferential selection of a metal ion or group of metal ions being thrown out of solution in a solid form, 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).

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. 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. Costly corrosion resistant materials such as stainless steel and polyplastics find wide applications in this respect.
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 aluminum (Al) is industrially and profitably extracted is bauxite (Al₂O₃.nH₂O). Bauxite is a mixture of aluminum hydrated oxides, with oxides of Si, Ti, and Fe as the main impurities. 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 (O₂) than carbon (C), and cannot be economically separated from O₂, by the usual pyrometallurgical methods. Aluminum oxide cannot melt below 2000°C, and is not reduced by heating with H₂; and heating strongly with carbon only produces the carbide, Al₄C₃. 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.

The Bayer process involves the extraction of aluminum by leaching finely crushed bauxite with strong caustic soda (30%) solution at high temperature (120-250°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, Al₂O₃.3H₂O (or Al(OH)₃, called gibbsite), or the monohydrate, Al₂O₃.1H₂O (or simply AlO(OH)), which consists of diaspore and boehmite. Operating within a certain temperature range (120 – 250°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°C) or stronger caustic soda or both. 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.

\[ \text{Al}_2\text{O}_3(s) + 2\text{NaOH}(aq) \rightarrow 2\text{NaAlO}_2(aq) + \text{H}_2\text{O} \]  

...(4)

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

Iron is precipitated as an insoluble ferric hydroxide

\[ \text{Fe}^{3+}(aq) + 3\text{OH}^-(aq) \rightarrow \text{Fe(OH)}_3 \]  

...(5)

and Ti as hydrated titanium oxide,

\[ \text{TiO}^{2+}(aq) + 2\text{H}_2\text{O} \rightarrow \text{TiO(OH)}_2 + 2\text{H}^+(aq) \]  

...(6)

while Si dissolves in the alkaline solution as Sodium Silicate

\[ \text{SiO}_2^{2+}(s) + 2\text{NaOH}(aq) \rightarrow \text{Na}_2\text{SiO}_3(aq) + \text{H}_2\text{O} \]  

...(7)

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

\[ 2\text{NaSiO}_3(aq) + \text{Na}^+(aq) + \text{Al(OH)}_4^{-}(aq) \rightarrow \text{NaAlSi}_2\text{O}_6(s) + 4\text{NaOH}(aq) \]  

...(8)

This forms part of the red mud or sludge commonly associated with Bayer’s process\textsuperscript{45,48}.

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

\[ \text{NaAlO}_2(aq) + 2\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3(s) + \text{NaOH}(aq) \]  

...(9)

\[ \text{Al(OH)}_3 \text{ seeds accelerate the nucleation and growth of the precipitated.} \]

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\textsuperscript{46}.

\[ 2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{H}_2\text{O} \]  

...(10)

Disposal of the Al residue is a major environmental problem associated with Al extraction and refining\textsuperscript{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, \([\text{Na, Ca)} (\text{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 \((\text{Fe, Mn)} \cdot (\text{Nb, Ta})_2O_5\), 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 \((\text{Nb}_2O_5)\), while the term tantalite is used for those containing over 50% \(\text{Ta}_2O_5\), depending on the ore and location\(^{44,53}\). \(\text{Ta}_2O_5\) and \(\text{Nb}_2O_5\) 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 \(\text{Nb}_2O_5\) and \(\text{Ta}_2O_5\) 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 \(\text{HCl}\) and \(\text{HNO}_3\) or HF to form anionic and fluoro-complexes of these metals: \(\text{NbOF}_5\)\(^{2-}\), \(\text{NbOF}_6\)\(^{2-}\), \(\text{NbF}_6\)\(^{2-}\), \(\text{TaF}_7\)\(^{2-}\) and \(\text{TaF}_8\)\(^{3-}\), etc\(^{3,41,42}\). Interestingly, the use of \(\text{HCl}\) 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 \(\text{HNO}_3\) within 120 minutes\(^{47}\).

\[
3 \text{ (Fe, Mn)} \cdot (\text{Ta, Nb})_2O_5 + \text{HCl} \rightarrow \text{TaCl}_6^- , \text{NbCl}_6^- \\
\text{or (Ta, Nb) Cl}_6^- + \text{FeCl}_3 \quad \text{...(11)}
\]

In the case of columbite containing tin, \(\text{SnO}_2\) dissolves as haloacids to give hexahalostannates:

\[
\text{SnO}_2 + 6 \text{HCl} \rightarrow \text{H}_2\text{Sn(Cl)}_6 + 2 \text{H}_2\text{O} \quad \text{...(12)}
\]

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\(^{50,51}\).

\[
3 \text{ (Fe, Mn)} \cdot (\text{Ta, Nb})_2O_5 + 8 \text{KOH} + (n-4) \text{H}_2\text{O} \rightarrow \\
\text{K}_8[(\text{Ta, Nb})_6\text{O}_{19,n}\text{H}_2\text{O})] + 3 \text{ (Fe, Mn)} \cdot \text{O} \quad \text{...(13)}
\]
K₈[(Ta, Nb)₆O₁₉.nH₂O] → 6 K (Ta, Nb) O₃ + 2 KOH + (n-1) H₂O  ...(14)

Reaction (30) may be expressed as follows:

[(Ta,Nb)₆O₁₉.nH₂O]₈⁻ → (Ta,Nb)₆O₁₉)₈⁻ + nH₂O  ...(31)

[(Ta,Nb)₆O₁₉]₈⁻ + H₂O → 6(Ta,Nb)O₅⁻ + 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, CuFeS₂, 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 SO₂ produced is converted to H₂SO₄ to be used locally for leaching processes.

The technique has been utilized in Duval’s CLEAR and Cyprus processes. The processes require leaching CuFeS₂ 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. who demonstrated that the method could become one of the most important means of exploiting mixed and polymetallic ores at relatively minimum cost.

\[
3 \text{ZnS} + 8 \text{HNO}_3(aq) \rightarrow 3 \text{Zn}^{2+} + 6 \text{NO}_3^{(aq)} + 3 \text{S}^0 + 2 \text{NO}_2(g) + 4 \text{H}_2\text{O} \quad \text{...(16)}
\]

\[
2 \text{CuFeS}_2(aq) + 2 \text{H}_2\text{SO}_4 + 2\frac{1}{2} \text{O}_2(g) \rightarrow 2 \text{CuSO}_4(aq) + 2 \text{FeOOH} + 4 \text{S}^0 + \text{H}_2\text{O} \quad \text{...(17)}
\]

\[
\text{CuFeS}_2 + 3 \text{FeCl}_3 \rightarrow \text{CuCl}_2 + 4 \text{FeCl}_2 + 2 \text{S}^0 \quad \text{...(18)}
\]

\[
\text{CuFeS}_2 + 3 \text{CuCl}_2 \rightarrow 4 \text{CuCl} + \text{FeCl}_2 + 2 \text{S}^0 \quad \text{...(19)}
\]
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:

\[ 2 \text{CuFeS}_2(s) + 4 \text{H}_2\text{SO}_4(aq) + 4 \text{O}_2 \rightarrow 2 \text{CuSO}_4(aq) + \text{Fe}_2\text{O}_3(s) + 4 \text{H}_2\text{O} + 3 \text{S}_0(s) \]  \[ \text{(20)} \]

Iron is usually precipitated as Fe(OH)$_3$, FeOOH or Fe$_2$O$_3$ 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 as shown by the following equations:

\[ \text{MS} + 2 \text{H}^+(_\text{aq}) \rightarrow \text{M}^{2+(_\text{aq})} + \text{H}_2\text{S}(_\text{g}) \]  \[ \text{(21)} \]

where \(M = \text{Fe}, \text{Zn}, \text{and Cu}\)

and

\[ \text{PbS} + 2 \text{H}^+(_\text{aq}) \rightarrow \text{PbSO}_4(_\text{s}) + \text{H}_2\text{S}(_\text{s}) \]  \[ \text{(22)} \]

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$_2$SO$_4$, 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$_2$SO$_4$ has a limited solubility. If the quantity of soluble Fe$^{2+}$ is not controlled, the following reaction may occur

\[ 6 \text{FeSO}_4 + x \text{H}_2\text{O} + 3 \text{O}_2 \rightarrow 3 \text{Fe}_2\text{O}_3.2 \text{SO}_3.x \text{H}_2\text{O} \]  \[ \text{(23)} \]

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.

\[ \text{PbS} + \text{H}_2\text{SO}_4(_{aq}) \rightarrow \text{PbSO}_4(_{s}) + \text{H}_2\text{S}(_{g}) \]  \[ \text{(24)} \]
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:

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

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 NH₄Cl, FeCl₃, FeSO₄, HCl, H₂SO₄, (NH₄)₂CO₃, 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 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 indispenability 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 Fe₂O₃, TiO₂, SiO₂, some hydrated sodium aluminium silicates, etc. About 400 million tonnes of this residue is produced annually world-wide⁷⁶,⁷⁷. Disposal problems are bound to arise, particularly in places where the technology of converting sulphur in sulphidic 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-piled 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 step¹⁸. 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 complete³²,², the processing of complex ores are advancing to a cleaner production with over 90% conversion⁴³-⁴⁶. 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 used⁷⁸,⁷⁹. Pollution problems associated with the treatment of certain ores with H₂SO₄ 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 H₂SO₄, 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 H₂SO₄ leaching¹. The fact that this does not happen implies that Ra (90%) precipitates from leach solution in the form of the insoluble, RaSO₄ 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$_2$SO$_4$ in this regard, as they form mostly soluble 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.

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