THE USE OF HYDROMETALLURGY IN TREATMENT OF SECONDARY RAW MATERIALS AND LOW – GRADE ORES

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Abstract

The available raw material types for metals production are primary high-grade ores, primary low – grade ores and secondary raw materials. Treatment of primary raw materials is often easier than treatment of secondary materials as the latter ones can have metals in combinations never found in nature. The basic phenomena in treating primary and secondary materials are the same. Thermodynamics and reaction kinetics are the same when applied to pure metals or compounds. The differences are in the complexity of the raw material that has strong influence on selectivity. Leaching of complex low – grade materials and secondary materials can result in higher chemical and energy consumption. The solution purification after leaching complex low – grade and secondary materials can also be technically more difficult than when operating with primary high – grade materials. This is due to higher number of metals in the solution. The origin of raw materials has no influence on production of metals from purified solutions.

Keywords: processing, minerals, secondary raw materials, hydrometallurgy, thermodynamics, electrochemistry

1 Introduction

In 2010 the European Union identified a list of 14 economically important raw materials, which are subject to a higher risk of supply interruption. The critical raw materials include antimony, beryllium, cobalt, fluorspar, gallium, germanium, graphite, indium, magnesium, niobium, platinum group metals, rare earths, tantalum, and tungsten. This is due to their high relative economic importance and high relative supply risk because of concentration of the production of certain raw materials outside EU. Materials of high economic importance that may become critical include aluminium, bauxite, chromium, iron, magnesite, manganese, molybdenum, nickel, rhenium, tellurium, vanadium, and zinc [1].

The available raw material types are primary high – grade ores, primary low – grade ores and secondary raw materials. Minerals are natural inorganic substances possessing definite chemical compositions and atomic structures. An ore is an accumulation of mineral in sufficient quantity for economic extraction. The minimum metal content required for a deposit to qualify as an ore varies from metal to metal. Many non-ferrous ores contain, as mined, less than 1 % metal. Gold may be recovered profitably from ores containing only 1 g metal per ton of ore. Iron ores containing less than about 45 % metal are regarded as of low – grade. Complex ores contain profitable amounts of more than one valuable mineral [2].

Primary high – grade ores are processed using tested technologies of extractive metallurgy. Production of steel using blast furnace, decarburisation and continuous casting, production of

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copper by flash smelting, converting and electrorefining, production of zinc by roasting, leaching and electrowinning, and production of aluminium by Bayer process and molten salt electrolysis all belong to this group. Primary low – grade sources either contain low amount of valuable compounds, the mineralogy of the ore prevents their easy liberation, or the ore contains impurities that prevent its utilization with known technology. Low – grade sources can be exploited with suitable technology [3]. Examples of low – grade ores are copper sulfide concentrates high in nickel, refractory gold ores, and black schist deposits.

Secondary sources can be considered as man-made raw materials having potentially high grade but also high complexity. Separation and recovery of materials from secondary sources is based on the same principles as those applied to primary sources. However, the recovery of materials from secondary sources can be more difficult because the feed is less constant and homogeneous than in primary metal – production. The man-made deposits are far more complex than natural deposits and they combine elements, which do not normally occur together in nature. Liberation process is more difficult due to more difficult size reduction as solid waste is considerably larger than minerals and shape variance in secondary sources can hinder effective separation [4]. The grade of useful and recoverable materials in the secondary sources is often higher, but the form of these can be more or less a composite structure, from which separation is difficult. Examples are rare earth elements that occur in nature in pegmatites but now in combination with other high technology metals like indium, germanium or gallium that in turn are found in base metal deposits. Thin film solar panels contain copper – indium/gallium selenide $Cu(In,Ga)Se_2$ on molybdenum. Molybdenum occurs together with copper in porphyry copper deposits, indium with zinc in sulfide deposits, and gallium in bauxite deposits [5]. When trying to reuse the products the technology is more challenging than mining.

“Urban Mining” is a term used for the process of reclaiming compounds and elements from products, buildings and waste. The background of the term is in the idea that a densely packed populated area is considered as a raw material source. The term denotes the systematic reuse of anthropogenic materials from urban areas that at the end of the product lifetime will become available for reuse. There is no general definition for urban mining, and it can describe exploitation of resources from landfills or traditional recycling of construction debris, scrap iron, plastics, or glass [6].

Most material cycles are rather complex and interconnected. For many metals there are different types of processes, which in many cases separate a large number of elements at the same time with various degrees of efficiency [7]. The mining of ores is the primary means of producing new metals for consumption. Ores are processed to concentrates with higher metal value and then processed to metals with wanted properties. Most of the base metals are easily recycled in the metallurgical plants after separation. The complex man-made sources, such as end – of – life vehicles and waste electronic and electrical equipment, require complete shredding and an initial separation of the materials into general type [8]. Then the individual metal-containing fractions can be processed to metals. Currently, the quality of recycled metals is often maintained through the addition of high primary metals and recovery without impurity dilution reduces the quality (or quantity) of recycled metals [9]. In many cases the recycled products contain valuable and rare elements in so small amounts and so tightly tied that profitable processing is not possible. In a worst – case scenario we may be heading to an era, where certain high – technology elements are used only once instead of the traditional large scale recycling of base metals. One of the large challenges is adopting new product design philosophy and use of alternative materials and constructions so that recycling will be possible. This will allow product-oriented materials sustainability, roughly outlined in **Fig. 1**, where end – of – life products are dismantled and recycled and only in exceptional cases discarded.

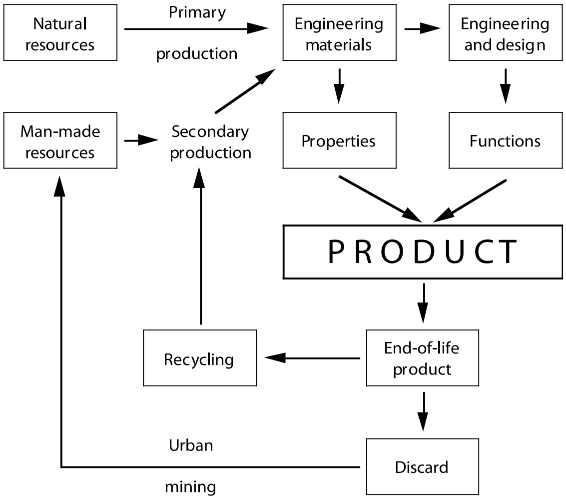

Fig. 1 Product – oriented material cycle including primary and secondary sources

Hydrometallurgy has traditionally been used in recovery of base materials by electrolysis, such as copper, lead, zinc and nickel, in the recovery of noble metals like gold and silver, and in the recovery of uranium and rare earth metals [10]. Some hydrometallurgical processes can treat effectively certain metals present in small amounts in the raw materials. An example of this kind of system is smelting and electrorefining of copper, where noble metals, As, Sb, Bi, Se and Te are recovered from anode slime. The most important feature of hydrometallurgical processes is their selectivity over pyrometallurgical ones [11] and this is the driving force for developing hydrometallurgical processes for low-grade and secondary raw materials. **Table 1** lists some raw material types processed by hydrometallurgical methods. There are similarities in processing of high-grade and low-grade primary raw materials and secondary raw materials. The general hydrometallurgical flow sheet will consist of similar unit processes. The thermodynamic and

Table 1 Various raw materials that can be treated by hydrometallurgical methods [11, 12]

Raw materials	**Examples**
Metals	Precious metals
Sulfides	Copper, nickel, zinc, lead
Oxides and hydroxides	Bauxite, nickel laterites, copper oxide ores, uranium ores, zinc ores and calcines, manganese ores and nodules
Complex oxides	Chromite, niobite – tantalite, pyrochlore, ilmenite, wolframite, scheelite
Selenides and tellurides	Anode slimes from copper electrolysis
Arsenides	Cobalt and nickel ores
Phosphates	Phosphate rock, monazite sand
Halides	Sodium, potassium, calcium
Spent catalysts	Noble metals, nickel, molybdenum, vanadium
Slags, sludge, dusts	Wastes from primary ferrous and non-ferrous metals production

kinetic laws are the same. There are also challenges that will be faced in processing of complex low-grade primary materials and secondary materials. Processing these materials is much more demanding than processing high-grade primary materials because at all process stages the separation of metals is more difficult, both by mechanical, chemical and physical methods.

2 General hydrometallurgical flowsheet

Extractive metallurgy has been defined as extraction of metals from naturally occurring compounds and refining them to marketable metals. This definition is too narrow as all raw materials are not natural compounds and all products are not metals [11]. In hydrometallurgy aqueous chemistry or ionic liquids are used to recover of metals whereas in pyrometallurgy thermal treatments are used for same purpose. A hydrometallurgical process consists of several stages, **Fig. 2**. The unit processes have certain aims and in Fig. 2 activation or pre – treatment and leaching aim to separation, solution purification aim is element transfer or compound formation, and product recovery aim is compound formation, metal production or metal purification [11].

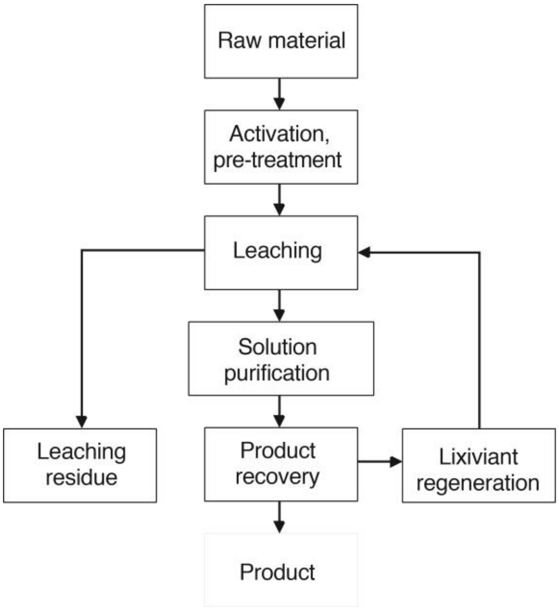

Fig. 2 Processing stages in a hydrometallurgical process flowsheet

The first requirement for leaching is that the raw material must be in physical form that allows contact between leaching solution and valuable metals to be leached. The properties of the raw material can be changed by physical and chemical methods. In the utilization of primary raw material comminution is used to liberation of the valuable minerals from the gangue minerals at the coarsest possible particle size. The object of mineral processing is to separate the minerals into two or more products with the values in the concentrates, the gangue in the tailings, and the locked particles in the middlings [2]. The valuable metal fractions are then subjected to leaching. For secondary raw materials the principle is the same, but the situation is more complex as there are more materials and they are often more tightly interlocked. If the chemo-mechanical pre – treatment is not effective enough, the feed to next process stages is comparable to middlings of primary raw material production and from that kind of material metal recovery is inefficient or even impossible.

In leaching solid materials are contacted by leach liquor capable of dissolving all or some of the metals. In leaching it is important that the dissolution is either selective so that only wanted metals are transported into solution or in case total dissolution is done the metals have so different properties that their separation is possible. The loaded or pregnant liquor is then subjected to a separation process for purification or recovery or both of desired metals or metal compounds. The product of a metallurgical product can be a concentrate, new compound, impure metal or purified metal or semi – product, **Fig. 3**. In all processing routes the separation of wanted and un – wanted fractions in the first mechanical or leaching stages is crucial.

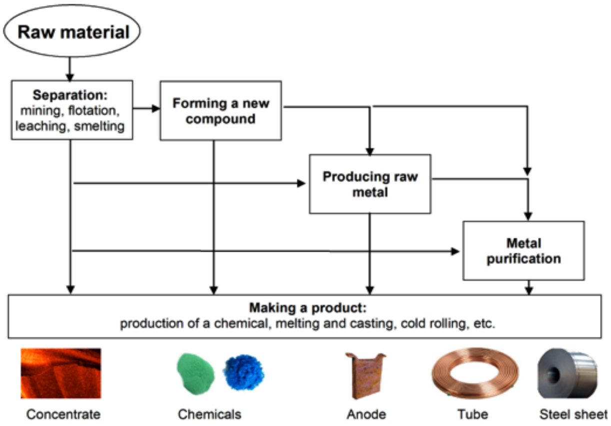

Fig. 3 Types of metallurgical products

2.1 Factors governing leaching

The dissolution mechanisms are physical, chemical and electrochemical [12]. In physical dissolution an ionic compound dissolves into solvent without changes in oxidation state. In chemical dissolution the dissolution of the compound is assisted by another compound in the solvent. In electrochemical dissolution the elements will oxidize or reduce because of oxidant or reductant in the solvent and the raw material structure breaks releasing the elements. In leaching the solution conditions must be such that the dissolved metal is thermodynamically stable. Thermodynamic conditions can be studied using for example solubility product, pH and redox potential (Pourbaix diagram), equilibrium potentials and mixed potential theory, and speciation. **Fig. 4** shows an example of Pourbaix diagram for copper sulfides. To release the metals it is necessary to select solution conditions in the acid and oxidizing region.

Table 2 shows thermodynamic standard electrode potentials for some reactions. The order of the potentials of reactions determines which one will oxidize or dissolve and which one will reduce. When using any cathodic reaction system it is capable to dissolve all systems with lower standard electrode potential. For example, ferric iron is capable to dissolve covellite CuS and all materials less noble than that. Hydrogen peroxide is capable to dissolve gold, but if the material is electronic scrap containing other metals, like copper, steel or zinc, those materials will dissolve preferentially. Hydrogen ion can dissolve many active metals even under reducing conditions.

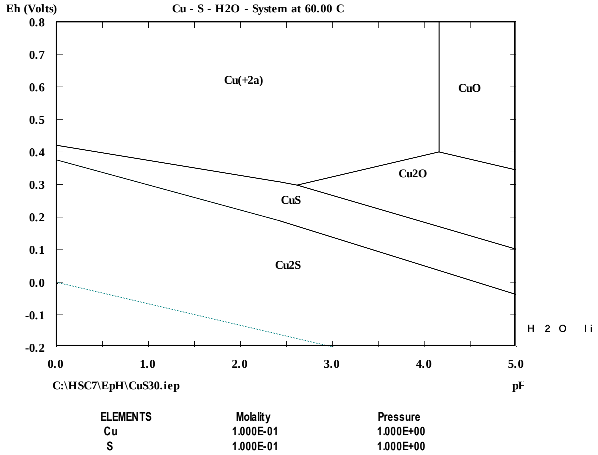

Fig. 4 Pourbaix diagram for leaching of copper sulfides

The theoretical treatment of electrochemical dissolution mechanisms was developed already in the 1930's. Most of the development work was done in relation to metallic corrosion. The research group of U.R. Evans in Cambridge determined the effect of anodic and cathodic reactions and their link to dissolution rates according to Faraday's law, e.g. [13 – 15]. Wagner and Traud presented the mixed potential theory in 1939 [16] and Mears and Brown introduced the concept of corrosion cell in 1941 [17]. The E-pH diagrams developed by Pourbaix became widely known in 1949 [18]. The graphical methods to show the dependence of electrochemical reactions known as the Evans diagrams for 70 years [13 – 15] were renamed to Ritchie diagrams in 2003 when they are applied in hydrometallurgy instead of corrosion science [19]. **Fig. 5** shows schematically the effect of anodic and cathodic reactions on dissolution rates.

Table 2 Standard electrode potentials of some anodic and cathodic reactions

Anode reaction	**E^o, mV**	**Cathode reaction**
$MnO_2 + 2\ H_2O = MnO_4^{2-} + 4\ H^+ + 2\ e^-$	2257	
	1776	$H_2O_2 + 2\ H^+ + 2\ e^- = 2\ H_2O$
	1501	$O_3 + 6\ H^+ + 6\ e^- = 3\ H_2O$
$Au = Au^{3+} + 3e^-$	1498	
	1395	$Cl_2 + 2\ e- = 2\ Cl^-$
	1228	$O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$
$Pt = Pt^{2+} + 2e^-$	1188	
	711	$Fe^{3+} + e^- = Fe^{2+}$
$CuS = Cu^{2+} + S + 2e^-$	616	
$Cu_2S = 2\ Cu^{2+} + S + 4e^-$	566	
$CuFeS_2 = Cu^{2+} + Fe^{2+} + 2\ S + 4\ e^-$	425	
$FeS_2 = Fe^{2+} + 2\ S + 2e^-$	390	
$Cu = Cu^{2+} + 2\ e^-$	337	$Cu^{2+} + 2\ e^- = Cu$
$ZnS = Zn^{2+} + S + 2e^-$	266	
	153	$Cu^{2+} + e^- = Cu^+$
$FeS = Fe^{2+} + S + 2e^-$	46	
	0	$2\ H^+ + 2\ e^- = H_2$
$Ni = Ni^{2+} + 2\ e^-$	-250	$Ni^{2+} + 2\ e^- = Ni$
$Fe = Fe^{2+} + 2\ e^-$	-440	$Fe^{2+} + 2\ e^- = Fe$
$Zn = Zn^{2+} + 2\ e^-$	-762	$Zn^{2+} + 2\ e^- = Zn$
$Al = Al^{3+} + 3\ e^-$	-1662	$Al^{3+} + 3\ e^- = Al$

Leaching conditions are selected so that the dissolved metal is thermodynamically stable. Dissolution reactions should be reasonable rapid. The conditions must be selected so that dissolved impurities and valuable metals can be separated from each other. In addition, the lixiviant solution must be able to be regenerated, and the lixiviant solution shall not be too expensive, corrosive or risky considering occupational health or environment. When leaching primary high – grade raw materials it is not too difficult to select suitable leaching conditions for sharp separation of wanted and unwanted metals. Primary low-grade materials are more difficult as the raw materials have much higher content of unwanted compounds and often the main task is to break down the valueless host mineral to reach the valuable ones. When leaching secondary materials the large number of metals can make leaching technically impossible, for example in oxidative leaching of electronic waste all other metals will dissolve easier than gold resulting in excessive chemical consumption.

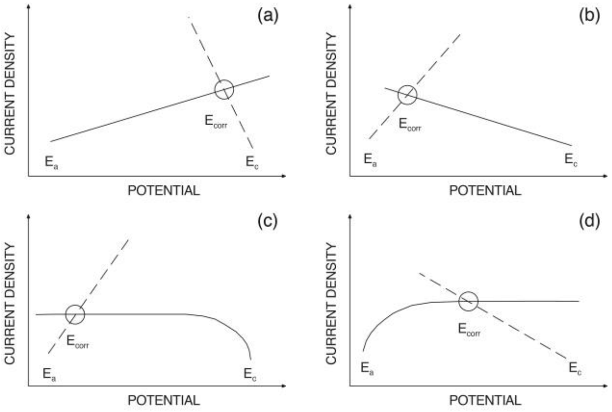

Fig. 5 Controlling factors in leaching described by Evans (Ritchie) diagrams: (a) Control by anodic reaction charge transfer; (b) cathodic reaction charge transfer; (c) cathodic reaction mass transfer; (d) anodic reaction mass transfer

Selection of the leaching technique depends on the grade of the raw material. Any leaching technique should produce as much wanted metals as possible, in shortest possible time, using as little as possible energy and reagents. Low – grade materials are processed using inexpensive heap, dump and vat techniques. Rich materials are processed using atmospheric reactors. Autoclaves are used when the product is so valuable that expensive technique can be feasible.

2.2 Solution purification

Solution purification is needed before final product recovery is possible. The purpose of solution purification is either to remove components that prevent recovery of wanted metal or to enrich wanted metal in a clean solution for recovery. Unit processes of the first group are crystallization, chemical precipitation, cementation and electrowinning. Unit processes of the second group are adsorption, ion exchange and solvent extraction, where the wanted metal is temporarily bound into a carrier material. Selection of purification process depends on solution properties, like type of harmful material and its concentration. Solution purification is based on differences of metal properties. Differences based on equilibrium include solubility, distribution between immiscible phases, equilibrium of chemical reaction, surface charge, and adsorption. Differences based on rate of a phenomenon are for example diffusion, ion mobility and formation rate of a compound.

The first solution purification method is solid-liquid separation. For primary raw materials the particle shape is more or less a sphere. For secondary raw materials all shapes are possible. Solid – liquid separation methods based either on sedimentation or filtration are more difficult to complete with irregular particles. The separation efficiency depends on particle size and shape and different sizes are separated with different efficiency.

For most metal – bearing solutions, chemical precipitation is the most effective means of removing dissolved metals. Chemical precipitation is based on changing the solution properties, usually concentrations of the compounds. Metals are usually precipitated as sparingly soluble hydroxides, sulfides or carbonates. Precipitation requires use of additional chemicals, sometimes also pH control, and additives to control growth, to break down complexes of wanted metals or to from complexes of unwanted metals. Too small additions of chemicals will not precipitate enough metals and too high additions will be waste of valuable chemicals. Hydroxide precipitation is generally used to remove large amounts of metal. Hydroxide deposits can dissolve back and often their handling is difficult. Ferrous iron hydroxides are particularly troublesome to filter. Theoretical equilibria for hydroxide precipitation are shown in **Fig 6**. Many metals have equilibria close to each other in the slightly alkaline range making selective separation difficult.

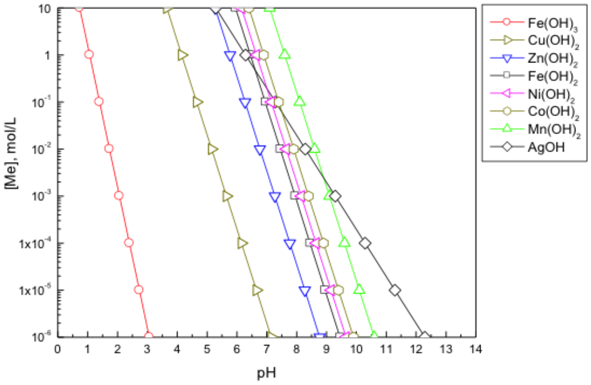

Fig. 6 Theoretical equilibria for hydroxide precipitation

Sulfide precipitation is another means of removing soluble metals from process streams. Sulfide precipitation produces more stable compounds than hydroxide precipitation. It is possible to get lower metal concentrations in the solution. Sulfide precipitation is more difficult than hydroxide precipitation because of the chemicals used. Precipitation is often done using hydrogen sulfide, sometimes sodium sulfide. **Fig. 7** shows examples of theoretical sulfide precipitation equilibria. As the precipitation is strongly dependent on sulfide concentration better selectivity is possible.

Iron is almost always present in raw materials and iron control can be troublesome due to its large amounts and difficult solution chemistry. Many trace elements can co – precipitate with ferric iron [20], and this can be problematic either as loss of valuable metals or as more demanding handling of solid waste. Sulfur compounds are also often present and the form of sulfur affects product recovery and tailings management.

In certain cases impurity metals can be removed by reducing them. The reduction is an electrochemical reaction and so a reducing compound like hydrogen or a less noble metal is needed. Metals can also be removed by electrolysis. In all these methods the most noble metals will deposit first, see Table 1. Scrap iron has long been used to deposit copper but generally metal reduction as solution purification method is suitable only for final polishing before metals recovery, like in zinc electrowinning. Hydrogen reduction is not useful for solution purification because of its high cost. Electrolysis is used in certain cases to control metal concentration and to remove noble metals. In primary raw materials extraction reduction is done in certain cases but in utilisation of complex, low-grade sources and secondary sources the potentially large number of different metals will again make the purification more demanding.

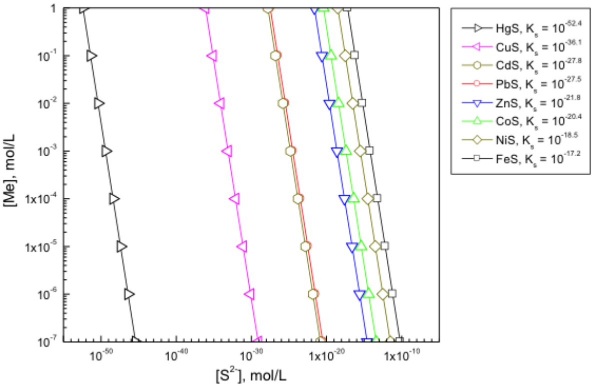

Fig. 7 Theoretical equilibria for sulfide precipitation

Solvent extraction and ion exchange involve a reaction between the contaminant species and a reactant or functional group in another phase (solvent extraction) or on a substrate surface (ion exchange) [20]. Both methods are selective and can operate continuously. Solvent extraction is better suitable for large amounts of metal and ion exchange for dilute solutions. Both methods are used in primary raw material extraction and they will likely become a main purification method in handling solutions from secondary raw materials leaching. Adsorption is the preferential partition of a solute at a solid-liquid interface [20]. Since the reactions take place at the substrate-solution interface, the adsorption capacity is proportional to the substrate surface area and the functional group density. Carbon is used in water treatment for removing organic contaminants, recovering gold from cyanide leach solutions, and activated carbons has been used to remove Cr(VI), Pb, Hg, Mo, Cu, Pb, Ni, and Zn. Adsorption works with dilute solutions but the selectivity can be difficult to control.

The purpose of solution purification is to remove impurities before recovery or to increase the metal concentration of the solution. Several unit processes are available, and some of them are based on transfer of the dissolved metal from one liquid phase to another while others are based on formation of a new solid phase. For the selection of solution purification unit processes the order of preference is:

- Crystallization, chemical precipitation or solvent extraction
- Cementation or ion exchange
- Electrolysis or adsorption

In selection of the solution purification method selectivity is a key issue. Selectivity in purification of solutions from primary high-grade materials has been worked out and tested over the years. Purification of solutions from complex low – grade primary materials is more demanding as there will be higher proportion of unwanted metals (like iron) and solution purification should not cause any of the valuable metals to end in waste. Purification of solutions from low – grade primary and secondary raw materials leaching will require very selective methods.

2.3 Product recovery

The aim of product recovery is to produce metals and compounds with sufficient purity so that they are marketable. In product recovery the selection of method is no more dependent on the raw material source. Product recovery from purified solution can use any of the precipitation or reduction methods. **Fig. 8** shows the main metal recovery methods. Crystallization and ion precipitation can be used for concentrated solutions to remove large amounts of metal. Precipitation can also be used for dilute solutions. Cementation is done for dilute solutions to recover metals. In this method a less noble and less expensive metal is needed and this will limit the number of applications. Gaseous reduction and electrolysis produce pure metals and both methods are tested for many metals.

3 Discussion

The use of hydrometallurgy in utilization of primary raw material sources has started in 1880's with the invention of cyanide method to recover gold and Bayer process to produce alumina from bauxite [10]. As the mining and processing techniques have improved progressively lower grade ores can be treated economically. For example during California Gold Rush of the 1850s, gold ores with 310 – 620 g/t were economically processed from placer deposits. With cyanidation and heap leaching gold ores with 0.8 g/t can now be treated [8]. Extraction of metals from low – grade raw materials produces large amounts of was that has to be treated as well. One of the benefits in utilization of secondary materials is the smaller volume of waste.

Treatment of primary raw materials is can be easier than treatment of secondary materials as the latter ones often have metals in complex combinations never found in nature. The basic phenomena in treating primary and secondary materials are the same. Thermodynamics in leaching, solution purification and product recovery does not change. Reaction kinetics in separation and recovery processes are the same when applied to pure metals or compounds. The main difference in treating low – grade and secondary materials are their higher complexity. Leaching of complex low – grade materials and secondary materials can result in higher chemical and energy consumption, for example because higher amount of unwanted materials has to be broken down in orders to reach the wanted compounds.

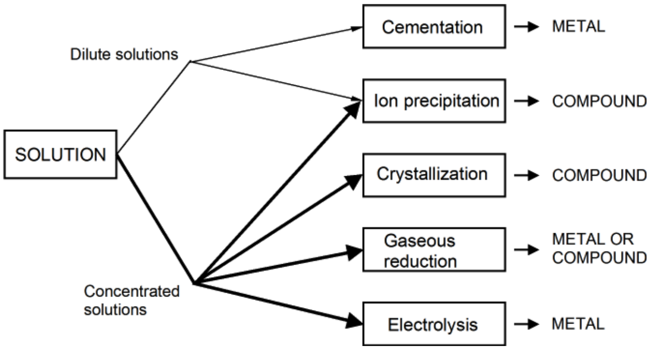

Fig. 8 Methods for recovering metals from solution

The solution purification after leaching complex low – grade and secondary materials can also be technically more difficult than when operating with primary high – grade materials. This is due to higher number of metals in the solution. In processing of primary high-grade materials the solution purification is often done by precipitating unwanted elements. In processing of low – grade primary and secondary materials the strategy may well be selective removal of wanted elements one at a time. In product recovery the selection of method is no more dependent on the raw material source. Product recovery from purified solution can use any of the precipitation or reduction methods.

4 Conclusions

The thermodynamic and kinetic principles are the same in treating primary high – grade, primary low – grade and secondary materials. The differences are in the complexity of the raw material that has strong influence on the selectivity of leaching. Pre – treatment of low – grade and secondary raw materials before leaching can be more demanding than that of high – grade materials. Leaching of complex materials can result in higher chemical and energy consumption. In selection of the solution purification method selectivity is a key issue. Purification of solutions from complex low – grade primary materials and secondary materials will require very selective methods as there will be higher proportion of unwanted metals and solution purification should not cause any of the valuable metals to end in waste. In product recovery the selection of method is no more dependent on the raw material source. Product recovery from purified solution can use any of the precipitation or reduction methods.

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