A Brief Review of Hydrometallurgical Methods in Extractive Metallurgy of Marine Ores

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Abstract

Marine surroundings (i.e., Seas and Oceans) constitute about 71% of the earth’s surface. It consists of an enormous reservoir of numerous mineral deposits such as massive sulfides, manganese nodules and cobalt-rich ferromanganese crusts. These mineral deposits could be a possible choice to satisfy the rising demand for raw materials and ores in the metal industry. Since 1960’s a variety of metallurgical processes (pyro/hydrometallurgical) have been developed to deal with marine ore deposits and extract different metals such as Au, Cu, Ni, Co etc. hydrometallurgical methods as proven technological treatments could be applied to the extraction of metals from concentrates (after pre-treatments like crushing, grinding, physical separation, flotation, etc.) or directly from crushed marine ores. In this paper, we briefly review developments of hydrometallurgical treatments (mainly leaching, modern bio-hydrometallurgical processes) of marine ores.

1. Introduction

Seas and oceans cover about 71% of the earth’s surface. They contain an enormous stock of various mineral resources such as sedimentary (marine placers), massive sulfide ore deposits, manganese nodules and cobalt-rich ferromanganese crusts. Sea and ocean floor ore deposits could make a contribution to marine materials in the metal industry. On this subject, more research and development appear to be required to ensure maximum benefit from marine resources of the marine environment. For the last five decades, a variety of mineral and metallurgical processes have been studied and developed to deal with marine ores and extract metals such as Au, Ni, Cu, Co, Mn, Sn, platinum group metals (PGM), Zr, Th, etc., from mineral deposits [1][2][3].

Generally speaking, there are two broad categories of mineral processing technology for marine minerals in terms of deposit structure, namely; technology for unconsolidated deposits (e.g., placer deposits), technology for semi-consolidated and consolidated (massive sulfide, manganese nodules, gold veins and cobalt-rich crusts) deposits. They may occur in a variety of forms, including beds, crusts, nodules, and at all water depths. To explain the extraction processes and recovery of metals from marine deposits, it is essential to have adequate information about physical/chemical properties and mineralogy of the deposits. The extraction techniques could be mainly divided into two major categories, i.e., low temperature hydrometallurgical and high-temperature pyrometallurgical treatments. The hydrometallurgical treatments include mainly leaching with various lixiviant (acids; e.g. HCl, H₂SO₄, etc.; basic medium; e.g. ammoniacal, etc.) and reducing reagents (e.g. pyrite, carbon, Na₂SO₃, etc.). Moreover, the modern bio-hydrometallurgical processes have been applied to marine ores (esp. Mn nodules) in several previous studies. [4][5][6]. Pyrometallurgical processes are undesirable because of the cost of removing the water content of nodules and crusts (up to 45%). In this paper, we focused on hydrometallurgical processes (due to their advantages over pyrometallurgical processes; e.g. energy consumption, environmental friendly, etc.) of marine ores. Firstly, marine ores and their properties would be discussed shortly and then the pre-treatments and hydrometallurgical processes of the marine ores would be explained in brief.

2. Marine Ores and Their Properties

Aforementioned, marine ores constitute of two main deposits in terms of deposit structure; i.e., unconsolidated
deposits (e.g., placer deposits), semi-consolidated/consolidated (massive sulfide, Mn nodules, Au veins and Co-rich crusts) deposits. Unconsolidated deposits include Au, Pt, cassiterite (SnO₂), titanium oxides (ilmenite, rutile), zircon (ZrSiO₄), monazite ((Ce, La)PO₄), diamonds, and a few others. Mineral deposits in this category include nodules, crusts, veins, and massive deposits, as of polymetallic sulfides [2], [5]. In this part of the paper, these types of deposits broadly categorized into two main groups, namely polymetallic massive sulfide ores and manganese nodules/cobalt-rich crusts.

2.1. Polymetallic massive sulfides

Since 1979, seafloor polymetallic sulfides have been found in the modern ocean floor at water depths ranging from about 1500 to 3700 m. Although only a small portion (less than 5%) of the world’s ocean ridge system has been explored in detail, about 20 deposits have been located in the Pacific Ocean, four in the Atlantic and one each in the Indian Ocean and the Mediterranean Sea. One of the largest deposits occurs in the Atlantis II Deep of the Red Sea. However, an evaluation of the economic significance of these deposits is limited by the lack of sufficient data concerning their distribution, size and bulk composition. Several individual deposits contain between 1 and 5 million tons of massive sulfide (East Pacific Rise 13°N, Hydrothermal Field) and only two deposits (Middle Valley and Atlantis 11 Deep, Red Sea) are known to contain considerably higher amounts of sulfides ranging between 50 and 100 million tones [4].

The mineralogy of these deposits mainly consists of varying proportions of pyrrhotite (Fe₁₋ₓS; x=0 to 0.2), pyrite/marcasite (FeS), sphalerite/wurtzite (ZnS), chalcopyrite (CuFeS₂), bornite (Cu₅FeS₄), barite (BaSO₄), anhydrite (CaSO₄) and amorphous silica (SiO₂). Massive sulfide deposits additionally may contain abundant galena (PbS), realgar (AsS), orpiment (As₂S₃) and locally native gold. Chemical analyses show that the seafloor deposits contain notable concentrations of Cu (1.3-5.1 wt. %) and Zn (4.7-34 wt. %) comparable to those of massive sulfide deposits on land. Gold and silver concentrations are locally high in samples from a number of deposits (up to 6.7 ppm Au and 1000 ppm Ag) and may reach concentrations of more than 50 ppm Au and 1.1 wt. % Ag in massive sulfides from back-arc rifts, which are dominated by felsic volcanic rocks. Precious metal contents of seafloor sulfides thus are well within the range of those found in land-based deposits [4], [5], [7].

An important project (i.e. Solwara project) which has been running on seafloor massive sulfide deposits in the Bismarck Sea (at total 19 regions in Papua New Ginea). The mineralogy of the deposit mainly consists of CuFeS₂ and ZnS, with subsidiary FeS₂, Cu₀Fe₄, PbS, Au and Ag. At Solwara-1 ore deposit, Cu is present almost exclusively as the CuFeS₂ and As is the only significant deleterious element in the ore. The average grade of valuable metals in this deposit (assuming all the regions) are as follows: Au: 15.5 g/ton, Cu 9.6% wt., Ag: 138 g/ton, Zn: 5.1% [8].

2.2. Manganese nodules/cobalt-rich crusts

The HMS Challenger Expedition of 1873-1876 discovered the black hydrous manganese dioxide concentrations, i.e., manganese nodules or in some sources polynematic nodules. The MnO₂ deposits were later called ferromanganese nodules due to their high iron content. Also these deposits could be used as an excellent source of Cu, Ni, Co and Mo. They are mostly found in the oceans basins of the world. The currently known distribution of manganese nodules and ferromanganese crusts on the ocean floor is based on information acquired by drill cores, dredged samples, seafloor photos, video camera records and direct observation from submersibles. Manganese nodules are comprised mainly of oxides of manganese and iron together with various metals were mentioned before. Goethite (FeO-OH) has been determined to be the most common iron-rich phase [9]–[12].

Nodules may contain up to 2.5% Cu, 2.0% Ni, 1.0% Co, 40.0% Mn, 27.0% Fe (all in wt.%), as well as smaller quantities of 22 other metals including Mo, Pb and Zn. Mineral-rich nodules are usually found at depths of approximately 4000 m or greater. The size of manganese nodules is dependent on the size of the nucleus, rate and duration of the accretion process, and burial of nodules after attaining a particular size. The sizes vary from micro nodules (<1 cm diameter) to nodules (> 1 cm < 15 cm diameter) and macro nodules (>15 cm diameter) [11], [12].

Moreover, ocean nodules have unique physical characteristics, which have very significant effects on the extraction of various metals from them. They are very porous (up to 0.62 by volume) and have a large surface area (up to 287 m²/g). Because of the considerable porosity, they contain a fair amount of water (usually about 30-40 wt.%, and due to this notable property, they consume the major part of the energy in the case of pyrometallurgical processes [11]–[13].

3. Pre-Treatment (Mineral Processing)

Mineral processing involves separating ore from worthless constituents and transforming it into intermediate or final mineral products. The number and type of steps involved in a particular process may vary
considerably depending on the characteristics of the ore and the end product or products to be extracted. Mineral processing encompasses a wide range of techniques from relatively straightforward mechanical/physical operations to complex chemical procedures [6], [14], [15].

In most cases, the first step in processing ores containing mineral grains is size separation. Generally, size separation could be needed to control the size of material fed to other equipment in the processing flow, reduce the volume of ore and/or produce a product of equal size particles. It is accomplished by use of various types of screens (e.g., trommel in case of coarser materials; sand and gravel) and classifiers (e.g. hydrocyclone in case of smaller particles). In case of unconsolidated deposits (e.g. placer deposits), the minerals are generally heavier than the silicate and other gangue with which they may be associated. Thus, traditional gravity separation methods (e.g., the silicate and other gangue with which they may be associated) are used to concentrate these kinds of ores. Moreover, magnetic separation techniques are used to separate minerals with magnetic properties (e.g. magnetite, ilmenite). Also, conducting minerals (e.g. rutile, ilmenite) may be separated from non-conductors (zircon, monazite) using electrostatic separation [2], [16].

Mineral deposits in the category of semi-consolidated/consolidated deposits include nodules, crusts, veins, and massive deposits, as of polymetallic sulfides. Processing of these minerals is likely to require crushing or grinding to reduce particle size, followed by chemical separation methods. In most cases flotation and/or other chemical processing (i.e., hydro/pyrometallurgy) are required to beneficiate the minerals [2], [16].

4. Hydrometallurgical Treatments

As previously mentioned, the high porosity of the manganese nodules results in high moisture content (30-40% by wt.), and this property results in the consumption of significant thermal energy in the case of pyrometallurgical treatments. As Agarwal et al [13] have pointed out, although manganese constitutes a major part of the nodules, production of manganese from the nodules can never compete with land-based dry manganese ores if the economy of extraction is taken into consideration. In such circumstances, the primary objective of nodules processing becomes extraction of minor but valuable metals associated with the Mn phase, such as Cu, Ni, and Co. Unfortunately, the concentration of Cu, Ni, and Co in the nodules across the oceans are found to be below 2%. At these low concentrations, pyrometallurgy is not an economically viable option. Moreover, hydrometallurgical processes do not emit any harmful gaseous effluents like most of the pyrometallurgical processes. Therefore, hydrometallurgy offers a probable process route here as in the case of other low-grade ores [11], [12].

Hydrometallurgical treatment refers to low-temperature leaching, purification and extraction processes. The hydrometallurgical treatments mainly include leaching with various lixiviant (acids; HCl, H2SO4, bases; ammonia leaching) with reducing agents (pyrite, carbon, coal, phenols, glucose, etc.) and modern bi-hydrometallurgical processes which studied mainly in Mn Nodules.

4.1. Leaching Processes

Two types of leaching processes can be considered; leaching by mineral acid and ammoniacal leaching. The parameters controlling both of these processes are mineralogy, pulp density and size fraction of the nodules, concentration of the leaching reagent, temperature and pressure of leaching, the presence and dosage of any reducing agent in the medium, pH of the medium (in the case of ammoniacal leaching), and time period of leaching [2], [12]. Hydrometallurgical extraction methods applicable to Mn nodules from the literature are summarized in Table 1.

Table 2. Summary of literature in the hydrometallurgical extraction of Mn nodules

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<tr>
<td>HCl</td>
<td>Na2SO4/Pyr- ite/Carbon, Propanol, Butanol, Coal</td>
<td>Ambient-98</td>
<td>75-92</td>
<td>[12], [17], [18]</td>
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<tr>
<td>H2SO4</td>
<td>Phenol/ Glucose/H2O/</td>
<td>1 min-6/ Ambient-160</td>
<td>90-99</td>
<td>[11], [12], [19], [20]</td>
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<tr>
<td>NH3/NH4+/ Cl</td>
<td>Glucose/ Reduction (400-700 °C)</td>
<td>2-6/ Ambient</td>
<td>80-90</td>
<td>[21]</td>
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4.2. Bio-Hydrometallurgical Processes

The period of modern bio-hydrometallurgy was initiated with the first patent on heap bio-leaching of Cu in 1958. However, the enlargement of bio-hydrometallurgy into the recovery of other metals came up only in the 1980s. Bio-hydrometallurgy is now being applied on a trading scale for the leaching of copper and the pretreatment of refractory gold ores. An enormous potential exists for bio-leaching and bio-beneficiation of a wide range of base metal and platinum group metals. However, there have been a very few cases of lab-scale studies on bio-
leaching of ocean Mn nodules, let alone the commercial application. Mn nodules can actually be viewed as a conglomerate of transition metal oxides having Mn (IV) and/or Fe (III) oxide as major phases. The valuable minor components such as Cu, Co, and Ni are disseminated within these two major phases by either adsorption mechanism or lattice-substitution. Mn reducing heterotrophs can be thought of as potential bio-leaching agents. Most of the Mn-reducing fungi and some of the bacteria reduce it non-enzymatically. A probable mechanism of the reduction can also be the production of metabolic products that act as strong reductants for Mn (IV) oxides [12].

5. Conclusion

Marine environment (i.e., Seas and Oceans) comprises more than 70% of the earth’s surface. It contains an excessive reservoir of numerous mineral deposits (i.e., unconsolidated, semi consolidated/consolidated mineral deposits). These mineral deposits could be an alternative to meet the rising demand for raw materials and ores in the metal industry. Hydrometallurgical methods as proven technological treatments could be applied to the extraction of metals from concentrates (after pretreatments like crushing, grinding, physical separation, flotation, etc.). In this paper, hydrometallurgical treatments, i.e., mainly leaching with lixiviant and reducing agents and modern bio-hydrometallurgical processes, briefly reviewed to extract metals (e.g., Cu, Au, Ag, Pt, Sn, etc.) and other valuable minerals and compounds from marine ores.

References