Challenges in the Metallurgical Processing of Marine Mineral Resources

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Abstract

In the deep sea, a gigantic stock of polymetallic raw-materials exists. These polymetallic raw-materials can be of high interest for the metal industry in order to satisfy the rising demands and needs of different metals. Especially the German industrial sector depends to an extensive amount on the import of raw-materials for the metal production.

During the past decades, a variety of processes have been developed to treat manganese nodules in order to extract mainly base metals like nickel, copper, cobalt or manganese. These processes mostly consist of different kinds of leaching of the manganese nodules and sometimes further treatment of the metal rich solution. Alternatively, pyrometallurgical processing steps are suggested during which a copper, nickel and cobalt rich metal phase and a ferromanganese or ferrosilicon manganese slag are produced. Other marine resources like massive sulphides are likely to be treated by conventional processes via beneficiation and smelting due to a comparable composition to chalcopyrite.

This paper describes the challenges in processing of marine mineral resources, especially manganese nodules, and states metallurgical concepts for their processing. In these suggestions, a major goal is reaching industrial input grades of intermediate products for an easy integration into commercial production routes of strategic and base metals. An additional target is to minimize metal losses throughout the entire process chain, such as optimizing the polymetallic resource efficiency. Furthermore an outlook on future investigations in the field of processing marine mineral resources with focus on high-tech metals is given.

The full paper will be published soon after the conference in a scientific journal.

1 Introduction

The German metal industry strongly depends on metal ore import due to the lacking or non-existing mining and storage sites. Therefore polymetallic mineral resources like manganese nodules, which can be found in German licence areas on the bottom of the Pacific Ocean, offer an interesting “new” resource to secure the future raw material supply. Hence, the economic and technical scientific interest in developing suitable process techniques for marine mineral resources is quite high.

2 Formation, Occurrence, and Composition of Manganese Nodules

Manganese nodules occur in depths of 4000 to 6000 m and form in the sediment due to the precipitation of different oxides out of the sea water. The growth of manganese nodules is slow (2 – 100 mm/million years). Their diameter varies between 1 and 15 cm and they show a layer structure. Their mineralogical composition is rather complex and they basically consist of different oxides and hydroxides. Figure 1 shows pictures of manganese nodules on the bottom of the ocean [1].

Figure 1: Manganese nodules in the sediment (left), sea cucumber above nodule area (right) [1]

One of the biggest and economically most important areas, where manganese nodules can be found, is situated between the Clarion- and Clipperton-Fracture Zones in the south of the Pacific Ocean. Different countries all over the world have used the opportunity to buy exploration licenses to evaluate potential mining technologies and retrieve nodules for research purposes; however, actual mining licenses do not exist at the moment. Germany holds two exploration licenses. An exemplary composition of manganese nodules can be seen in Table 1 [1,2].

Table 1: Exemplary element distribution in manganese nodules [1]

Element (average content)	Clarion-Clipperton Fracture Zone	Eastern GermanTerritory
Manganese (%)	25,4	31,2
Iron (%)	6,90	6,20
Copper (%)	1,02	1,17
Nickel (%)	1,28	1,36
Cobalt (%)	0,24	0,16
Titanium (%)	0,53	0,25
Molybdenum (µg/g)	520	604
Zirconium (µg/g)	350	300
Lithium (µg/g)	108	130
Tellurium (µg/g)	5,1	3,4
Niobium (µg/g)	34	19
Tungsten (µg/g)	76	65
Platinum (µg/g)	0,124	0,109
Cerium (µg/g)	428	249
Neodymium (µg/g)	112	128
Dysprosium (µg/g)	24	27

According to the Federal Institute for Geosciences and Natural Resources (BGR[1]), the existing one billion metric tons of manganese nodules contain 24 million metric tons non-ferrous metals. But, since a decent process for metal extraction still has to be found and the nodules arrive at the metallurgical processing plant with a residual moisture of at least 30%, as well as due to the fact that pyrometallurgical processing is usually high in energy input, nearly 60% of the overall processing costs have to be reserved for the metallurgical processing [3,4].

3 Suggested Processing of Manganese Nodules (State of the Art)

In the past, there has been extensive research about suitable process designs to extract metals out of nodules. However, the main focus was put on the extraction of base metals like Cu, Mn or Ni. When it comes to trace metals in manganese nodules, their distribution behaviour as well as their extraction has hardly been investigated.

Looking at the crystal structure of manganese nodules, it can be seen that Mn and Fe oxides form the matrix structure. The other valuable metals are present as oxides as well but substituted for atoms with a similar radius, in this case Fe or Mn. Thus, valuable metals like Ni, Cu, Co, Mo or V are integral parts of the matrix oxides. Particularly Co and Ni substitute for Mn, thus making it

[1] BGR – Bundesanstalt für Geowissenschaften und Rohstoffe

inevitable to break the MnO_2 or Fe matrix via reduction/cracking the crystal lattice to achieve good yields. Since the manganese content is rather high, also a potential Mn recovery has to be considered in the process design [5,6,7,8].

Leaching with ammonia (with an upstream roasting process to pre-reduce the valuable metals) has been regarded as one of the most promising treatment methods for metal extraction because it enables a selective leaching of Ni, Cu, Co and Mo without dissolving any Mn, Fe or the gangue. This process is based on the metallurgical treatment of lateritic nickel ores but can only be accomplished by adding reducing agents at high temperature (200 – 250 °C) and pressure (up to 50 bar). Leaching with sulphuric acid is seen as a cost-effective alternative to ammonia but with a high consumption of acid and slow kinetics. Using diluted hydrochloric acid as leaching agent is suitable if Mn and the associated metals (Ni, Cu, Co) are the target metals. The hydrogen chloride dissolves the otherwise insoluble MnO_2-matrixwithout dissolving any Fe. The so-produced chlorine salts have a positive effect on the subsequent electrowinning, but the ecologic aspect and the high investment and maintenance costs have to be kept in mind [4,5,8,9,10,11].

As a pyrometallurgical treatment of nodules, a reducing smelting operation in an EAF at 1000 °C with coal is suggested to slag and separate the gangue, Mn and partly Fe, and to produce an alloy of Ni, Co, Cu, and Fe. This so-produced slag has a Mn content of 35 – 40% and can be further processed to a ferromanganese product. A pyrometallurgical reduction in an EAF can also be a possible treatment for the leach residue (20% Mn) from the ammonia leaching process to produce ferrosilicon manganese which shows the required purity to be used as a deoxidizing agent in steel production. By adding coke, flux and the slag from ferromanganese production at temperature of 1400 – 1550 °C, a suitable product for the steel industry can be produced out of this residual waste. This is economically and ecologically worthwhile since it minimises the waste amount of the previous processes [5,9,12,13].

Manganese nodules are similar to lateritic nickel ores with respect to Cu and Mn content. Also the mineralogy is quite alike, as lateritic nickel ores also basically consist of oxidic-hydroxidic compounds. Hence, it is obvious and makes sense to base process developments on already existing processes for lateritic nickel ores. The following Figure 3 shows a flow sheet of a recommended process based on a treatment for lateritic nickel ores for metal extraction out of manganese nodules. In this process, the nodules are leached after reducing/separating the Fe and Mn and converting the rest into a Cu-Ni-matte phase. The slag produced in the EAF acts as a collecting phase for oxygen-affine metals (Mn, etc.). Compared to direct leaching processes, only 5% (instead of 100%) of the nodules are leached. This enables smaller equipment dimensions (and consequently lower costs), a lower environmental impact and fewer leaching residues. However, the energy consumption is not negligible, as the nodules are dried, reduced, melted, roasted and then leached [6,10].

Figure 3: Simplified flow sheet of a suggested process proposed by INCO Ltd. [6]

4 Outlook on Future Research

Together with the Federal Institute for Geosciences and Natural Resources (BGR) and the Unit of Mineral Processing (AMR[2]) at RWTH Aachen, the IME[3] has recently started a research project on developing suitable process chains and process steps for the metal extraction of valuable and critical metals out of marine mineral resources with a special focus on manganese nodules. The first part of this research includes an international literature study, to identify conditioning and extraction technologies for manganese nodules as well as identifying the behaviour and distribution of critical metals such as molybdenum, vanadium, tellurium, etc., during conditioning and metallurgical processing. Therefore, the initial experiments will assess existing process designs (e.g., INCO Process) regarding their ability to recover critical metals.

The already conducted literature research showed that for an optimum exploitation of this polymetallic "ore" it is indispensable to not only choose hydro- or pyrometallurgy, but to develop a

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[2] AMR – Lehr- und Forschungsgebiet Aufbereitung mineralischer Rohstoffe der RWTH Aachen

[3] IME – Institut für metallurgische Prozesstechnik und Metallrecycling an der RWTH Aachen

process that combines both. As described, the main focus in the past was the extraction of major metals like Cu, Mn, Ni or even Co. However, as it is essential to not only extract these, but also critical metals, further research is needed.

Additionally, process technology has improved over the past few years and the global understanding of closed-loop and zero-waste has increased. This implies that, even if the outcome of future research is a rather unconventional process for metal extraction out of marine mineral resources, this process might have a chance to establish.

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