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Pyrometallurgical extraction of valuable metals from polymetallic deep-sea nodules

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Abstract

The steadily growing demand for critical metals and their price increase on the world market makes the mining of marine mineral resources in the not too distant future probable. Therefore, an enormous focus lays currently on the development of a viable process route to extract valuable metals from marine mineral resources such as polymetallic nodules. These nodules contain industrially important metals like nickel, copper and cobalt in substantial amounts. For a country with few natural resources like Germany the industrial treatment of marine mineral resources could lead to a significantly decreased dependence on the global natural resource market. Especially a reduced dependence on geopolitical volatile supplier countries like the DR Congo, which is the country with the largest supply of cobalt ore globally, may be achieved. Moreover, the recovery of other technology metals such as molybdenum, vanadium or rare earth metals may be possible from manganese nodules.

The nodules used were supplied by the BGR, German Federal Institute for Geosciences and Natural Resources, and have origin in the German licensed territory of the Clarion Clipperton Zone in the Pacific Ocean. This paper presents recent metallurgical research to extract metal values from these nodules. Current studies further the extensive research on marine resources of the 1970’s. However, recently other technology metals (Mo, V, REE) have come more and more into focus. The development of a general metallurgical process route to treat nodules is challenging due to varying nodule compositions. Especially challenging is a high Mn content, since the liquidus temperature of a smelted slag phase directly correlates with Mn content.

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

1 Introduction

The exploitation of polymetallic deep-sea nodules, as depicted in Figure 1, from the deep sea has once again become a political and economic topic in recent years. Many countries have purchased exploration rights for territories in the Clarion Clipperton Zone south of Hawaii from the International Seabed Authority (ISA). The main focus of the processing of these nodules lays on the extraction of the industrial metals nickel, copper and cobalt. The nodules would serve as an enormous reserve for these metals, since they are found in relative abundance. For example, the nodules constitute an estimated reserve of up to 290 million tons of nickel and up to 60 million tons of cobalt. These estimated amounts currently surpass common land based reserves in mines for nickel, cobalt and manganese (see [2][3]). Additionally, other valuable metals such as Molybdenum and Vanadium are found in relatively high concentrations. Thus, an extraction or at least enrichment in a marketable by-product of these metals should also be pursued.

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 ferro-manganese 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.

Figure 1: Left: Polymetallic nodule from the Pacific Ocean (~ 6 cm, left)
Right: Nodules on the ocean floor at 4000-6000 m depth [1]

2 Nodules Composition and Applied Thermochemical Models

The nodules used in this study origin in the German licensed territory in the Pacific. In total 206 nodule samples were analysed by ICP-OES and -MS measurements. Table 1 shows that on average their manganese content is significantly higher than the nodule samples, which were studied in the

1970's. The table further highlights, that a metallurgical process to treat this kind of raw material has to be flexible in dealing with varying nodule compositions. Therefore, a batch process would be ideal, since process parameters could be adjusted for each separate batch of nodules. The differing composition of the nodules studied here leads to a number of challenges:

1. Increased liquidus temperature of a slag phase
2. Resulting higher reduction temperature
3. Differing basicity of the slag

Table 1: Chemical composition of nodules from German territory (BGR samples) in comparison to literature nodule compositions from different regions

wt.-%	**BGR samples**	**Sridhar et al.** [4]	**Haynes et al.** [5]	**Han et al.** [6]
Mn	31.23	23.20	21.60	20.03
Fe	6.20	6.90	10.4	16.99
Ni	1.36	1.14	0.90	1.26
Cu	1.17	0.80	0.66	0.80
Co	0.16	0.22	0.26	0.37
Mo	0.06	0.06	0.04	0.04
V	0.06	0.04	0.05	n/a
Zn	0.15	0.11	0.11	n/a
Al	2.27	3.07	2.80	2.01
Mg	1.93	1.75	1.53	n/a
Si	5.90	8.60	7.72	8.97
Ca	1.62	1.29	2.12	1.64
Na	2.03	3.80	2.20	n/a
K	0.99	n/a	0.87	n/a
Ti	0.25	0.39	0.73	n/a
MnO/SiO_2	**3.19**	**1.63**	**1.69**	**1.35**

The main mineral phases of manganese nodules are complex, fine grained, often metastable, poorly crystallized and mostly nonstoichiometric (see [5]). Particle sizes vary, but are generally approximately 0.01 µm, highlighting why physical processing to enrich metal values is very difficult (see [2]). The most common minerals in ocean nodules are todorokite or 10 Å manganite (buserite), birnessite, vernadite and different iron oxides (mostly goethite and feroxyhyte) (see [5][7]).

A look at the quasi binary phase diagram of the main nodule constituents MnO, SiO_2, FeO, Al_2O_3 and MgO (Figure 2) clearly illustrates how significantly the ratio of MnO to SiO_2 influences the liquidus temperature of the slag. This phase diagram was created using the "Phase Diagram" module of FactSage™ 6.4. The diagram takes a constant fraction of FeO (12 wt.-%), Al_2O_3 (6 wt.-%) and MgO (5 wt.-%) into account. The resulting MnO/SiO_2 ratio is modelled as the x-axis. It should be noted however, that these five oxides do not represent the complete nodule composition (approx. 87 %) and the generalization is therefore simplified.

The approach to pyrometallurgical metal winning from polymetallic nodules was developed by Sridhar et al. (see [4][8]). The nodules are crushed dried and pelletized to be pre-reduced in a kiln. In the first smelting step the pellets are fed into an electric arc furnace (EAF), where a manganiferous slag is produced from which an iron, nickel, copper metal phase is carbothermically reduced at 1380 to 1420 °C. Thus, the main manganese stream is separated from the valuable metals. [4]

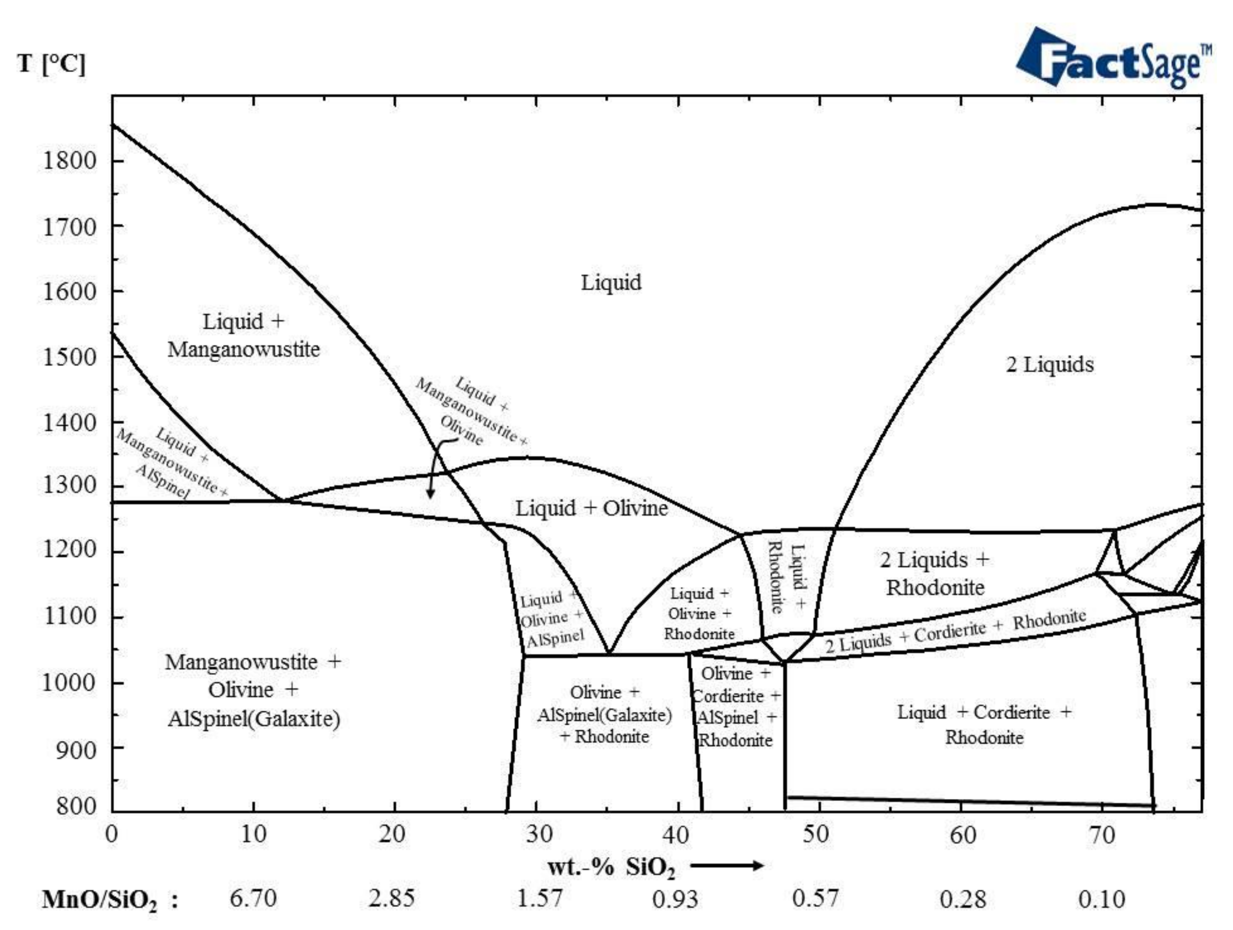

Figure 2: Quasi binary phase diagram of the five main oxides (MnO, SiO_2, FeO = 12 wt.-%, Al_2O_3 = 6 wt.-%, MgO = 5 wt.-%)

The main goal of the research presented here is to constitute the slag, so that Mn is held in the slag for further MnFe(Si) production and to maximize the Ni, Cu, Co and Mo reduction. To minimize the reduction of manganese from the slag the reduction temperature must be below approximately 1500 °C (depending on MnO activity in the slag), because at higher temperatures carbothermic reduction of MnO is thermodynamically possible. Due to the fact that the Mn content of the nodules studied here is significantly higher than to those studied in the 1970’s (compare Table 1), the liquidus temperature of the autogenic slag is considerably higher, as illustrated in Figure 2. Therefore, the metal reduction must take place at high temperatures so that more manganese is undesirably reduced. This could be shown in FactSage™ models and was verified experimentally. Thus, the research has shown that it is meaningful to treat nodules in a batch process and to adjust the MnO/SiO_2 ratio according to each composition.

3 Experimental Work and Results

All experimental work was conducted in a lab-scale electric arc furnace (EAF) at IME (RWTH Aachen University). The furnace is equipped with a 50 kW DC power supply and a single graphite top electrode.

The counter electrode is a water cooled copper block at the bottom of the furnace. The set-up is schematically illustrated in Figure 3. The experiments were mainly carried out in a graphite crucible. Yet, to minimize the carbon uptake of the reduced metal phase an alumina, chromium(III) oxide refractory lining was also used, which proofed very stable against the slag. The charging of the pellets was done by hand. The position of the top-electrode was likewise adjusted by hand. After all material had been charged into the crucible, the electrode was submerged into the slag to allow carbothermic reduction (SAF operation). The effects of reduction time were evaluated by taking slag samples during the experiments. After tapping the metal and slag phases were separated and analysed by XRF.

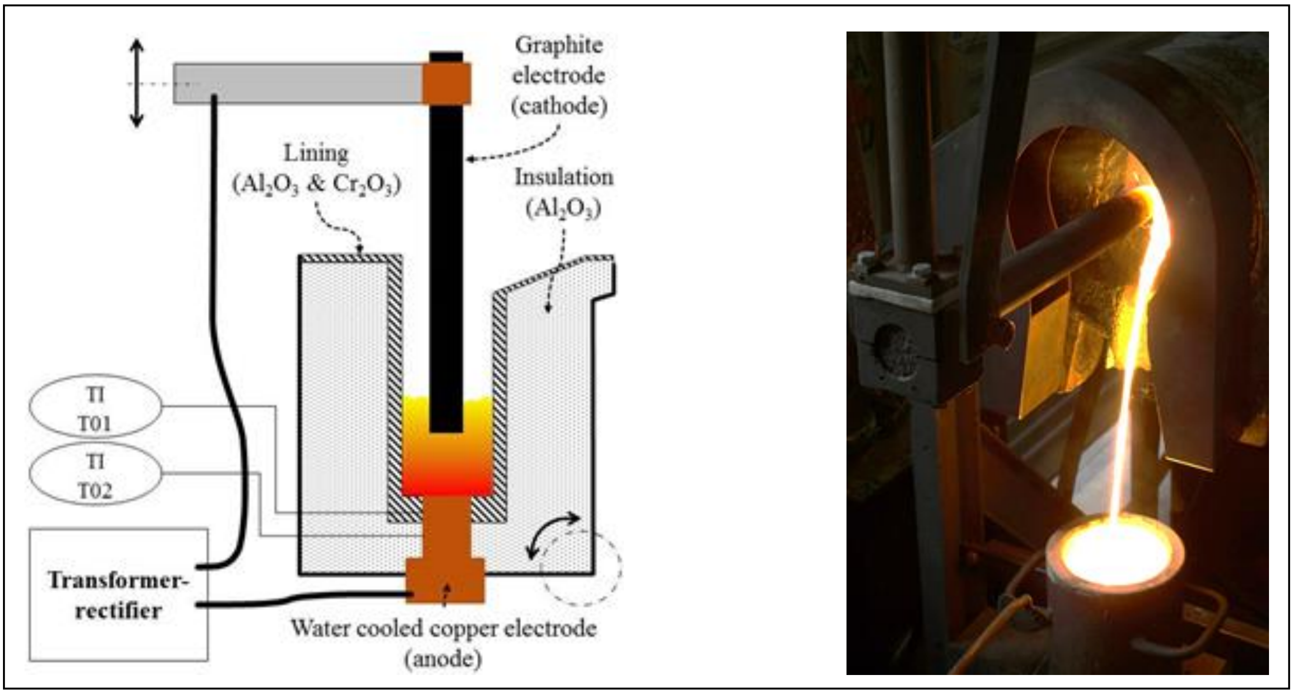

Figure 3: Left: Schematic of the lab-scale EAF at IME (approx. 6 L melt volume)
Right: Tapping of the slag at approx. 1450°C into a steel mould

In total 10 trials were conducted. SiO_2 was added as flux and pelletized with ground and dried nodules. Different MnO/SiO_2 ratios as well as reduction times were evaluated. The average reduced metal composition is illustrated in Figure 4, which shows excellent compatibility to FactSage™ models as well as published research (see [4][9]). The tapping of the slag and metal phases is depicted in Figure 3.Temperature control has proved to be critical for the reduction as is substantiated by theory, but is very challenging to control in this experimental setup. Overheating of the slag and foaming are a problem. Per experiment roughly 3 kg of feed material were used. However, physical losses due to dust and splashing of the liquid slag were high.

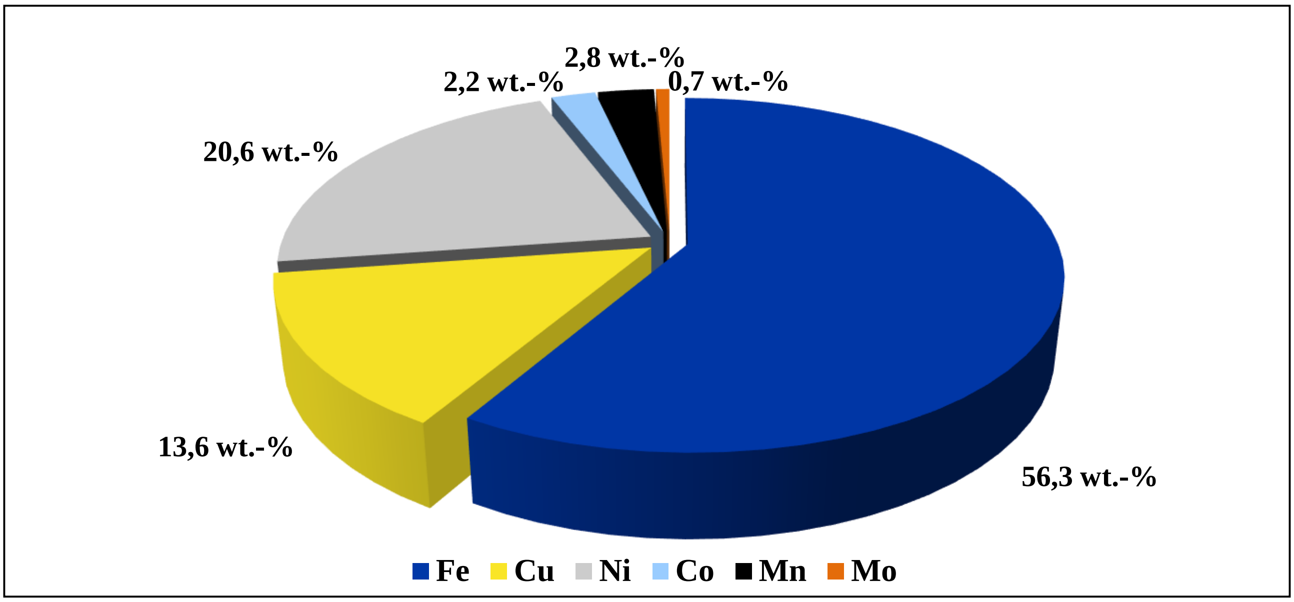

Figure 4: Average composition of reduced alloy

The main goals in this smelting and reduction step are on the one hand to reduce all valuable metals (Ni, Cu, Co, Mo) into an iron alloy and to hold manganese in the slag for further ferro-manganese reduction at higher temperatures (> 1600 °C). Recovery rates for Ni, Cu and Co exceeded 90 %, but Mn content of the alloy increases with MnO activity in the slag. Thus, the MnO/SiO_2 ratio of the feed material proved to be a critical process parameter, which should be below 2, depending on desired slag characterization (i.e. basic or acidic). Mo recovery was in most cases also above 90 % but varied. The slag basicity was evaluated using equation (1) (see [10]). However, it should be noted that this basicity equation was presumably not designed for high MnO contents as is found in the slags here. Therefore, a revaluation of a new basicity equation may be worthwhile and will be subject to further research. Yet, as a first approximation to characterize the resulting slags the values for the basicity obtained by eq. (1) were suitable.

$$B = \frac{\%(CaO) + \propto \cdot \%(MgO) + 2{,}0 \cdot \%(MnO)}{\%(SiO_2) + 0{,}6\,\%(Al_2O_3) \cdot \left[\frac{\%(CaO) + \propto \%(MgO)}{\%(SiO_2)} - 1{,}19\right]} \qquad \text{with } \propto = \frac{1{,}84\,\%(SiO_2) - 0{,}9\,\%(CaO)}{\%(SiO_2) + 0{,}9\,\%(MgO)} \qquad (1)$$

The consideration of the MnO/SiO_2 ratio has proved very useful to characterize a pyrometallurgical process to treat manganese nodules. It is immensely important for a metallurgical process to have a rather unvarying feed material, which is why a constant MnO/SiO_2 ratio between 2 and 1.5 would be ideal. In an industrial process this could easily be accomplished for each batch of nodules. The reduction times were varied after all material had been charged into the crucible and a homogeneous melt was formed, after which the top-electrode was submerged in the liquid slag for 20 minutes to 40 minutes (SAF operation). During that reduction time slag samples were taken in 5 minutes intervals.

4 Conclusions

The recent experimental work supported by thermochemical modelling has shown that the first carbothermic reduction step for the metallurgical treatment of polymetallic manganese nodules is very critical. A pyrometallurgical process is favourable to hydrometallurgical treatment of nodules, when the extraction of base metals is the main focus. Pyrometallurgical operations can easily treat thousands of tonnes of nodules per batch in an electric arc furnace. Whereas hydrometallurgical operations would require enormously large volumes, have need of large acid or base volumes and result in large waste water volumes as well as tailings. However, nickel, copper, cobalt and molybdenum are readily reduced from a carefully designed slag. Recovery rates for all metals exceed 90 %. Through careful temperature control of the slag during reduction, manganese reduction can be avoided so that an alloy with less than 3 wt.-% Mn is possible (see Figure 4). A significant Si uptake of the alloy even at high silica additions could not be detected. This could be shown experimentally and verifies published research (see [4][8][9]). The removal of iron from the alloy may subsequently be done by pyrometallurgical conversion with a fayalite slag. The alloy conversion as well as further MnFe production will be investigated in future research. Additionally, up-scaling experiments are planned, if raw nodules and further funding can be acquired.

Special acknowledgements for the support of the work and supply of nodules go to BGR.

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