Optimized, zero waste pyrometallurgical processing of polymetallic nodules from the German CCZ license area

David Friedmann[1], Bernd Friedrich[1], Thomas Kuhn[2] and Carsten Rühlemann[2]

[1] IME Process Metallurgy and Metal Recycling
RWTH Aachen University
Intzestr. 3, 52072 Aachen, Germany
(Corresponding Author David Friedmann: dfriedmann@ime-aachen.de)

[2] BGR Federal Institute for Geosciences and Natural Resources
Stilleweg 2, 30655 Hannover, Germany

INTRODUCTION

This paper explores the option of direct reduction smelting of the nodules from the German license area in the equatorial NE Pacific in a submerged arc furnace (SAF). An optimized slag design is proposed to separate the larger Mn-bearing stream from the valuable metals (i.e. Ni, Cu, Co, Mo). The slag optimization allows a maximum of Mn to be retained in the manganese-silicate slag on the one hand and a maximized metal recovery in a FeNiCuCo alloy on the other. This way, the goal is to make use of the complete nodules ("zero-waste") instead of extracting only the metals Ni, Cu, and Co, which make up about 3 wt%. The process closely relates to the "Inco Process" by the Ocean Management Inc. (OMI) of the late 1970s, which was a consortium of INCO (International Nickel Company, CAN; today Vale Canada), Preussag AG & Metallgesellschaft AG (GER), DOMCO (JPN), and Sedco (USA). However, the manganese containing slag is investigated in more detail to recover FeMn, FeMnSi and/or SiMn. To optimize the process modern tools such as thermo-chemical modeling in FactSage™ have been used. [1,2]

Polymetallic deep-sea manganese nodules may offer a decreased dependency of raw material imports for Germany and the EU. Currently, four European countries (United Kingdom, Belgium, Germany, and France and an Eastern European consortium (InterOcean Metal)) hold exploration licences for these nodules in international waters in the equatorial NE-Pacific. The license areas each cover 75 000 km^2 of the seafloor and are located in the Clarion Clipperton Fracture Zone (CCZ) south east off Hawaii at water-depths between 4000 and 6000 m. The nodules may be used as a resource for industrially important metals such as Cu, Ni, Mn as well as for technology metals like Co, Mo, V and Zn. The average chemical composition of nodules from the German license area is presented in Table 1. [3,4]

Table 1. *Average chemical contents of wet nodules from the German license area (LOI ~ 20%, mainly water) and converted into basic metal oxides ("dry", adjusted to 100%, Fe^{2+}/Fe^{3+} = 0.8/0.2 assumed as in slag) [3]*

	Mn	**Fe**		**Si**	**Al**	**Na**	**Mg**	**Ca**	**Ni**
wt%	31.22	6.20		5.90	2.30	2.03	1.90	1.60	1.36
Oxide	**MnO**	**FeO**	**Fe_2O_3**	**SiO_2**	**Al_2O_3**	**Na_2O**	**MgO**	**CaO**	**NiO**
wt%	50.51	8.00	2.22	15.82	5.45	3.43	3.95	2.81	2.17
	Cu	**K**	**Ba**	**Ti**	**P**	**Co**	**Zn**	**Mo**	**V**
wt%	1.17	0.99	0.44	0.25	0.16	0.16	0.15	0.06	0.06
Oxide	**CuO**	**K_2O**	**BaO**	**TiO_2**	**P_2O_5**	**CoO**	**ZnO**	**MoO_3**	**V_2O_5**
wt%	1.84	1.49	0.62	0.52	0.46	0.25	0.23	0.11	0.13

The average concentration of nodules on the seafloor varies greatly, but on average the abundancy in the CCZ is 15 kg/m^2. Currently, the estimated "commercially exploitable" zones in the German concession hold ca. 175 million tonnes of nodules. The pre-dominant minerals found in nodules are complex, non-stoichiometric Mn-oxides and hydroxides (Birnesite, Buserite, Vernadite [5]). These mineral particles are extremely fine-grained (< 1 µm) and inter-grown, the valuable metals (Ni, Cu, Co, Mo) are mainly located in the MnO_6-octahedra of the mineral matrix. Thus, the mineral matrix must be broken down, e.g. by leaching, thermal upgrading or melting, to liberate these metals. Whereas classic beneficiation techniques fail to provide a metal-concentrate. [4,6]

ADAPTED ZERO-WASTE PROCESSING SCHEME

The research presented here deals with the development of a sustainable, zero-waste (pyro) metallurgical process to treat polymetallic nodules. The aim is furthermore the generation of a Mn-product as ferro-manganese as well as a Ca-Si product, which have been neglected in the past, while ensuring a complete recovery of the valuable constituents Ni, Cu, and Co.

Original process designed by OMI consortium

The process is based on research of the late 1970s by the German-Canadian (Preussag, Metallgesellschaft, INCO) Ocean Management Inc. (OMI) consortium. Figure 1 shows the original process developed by the OMI consortium.

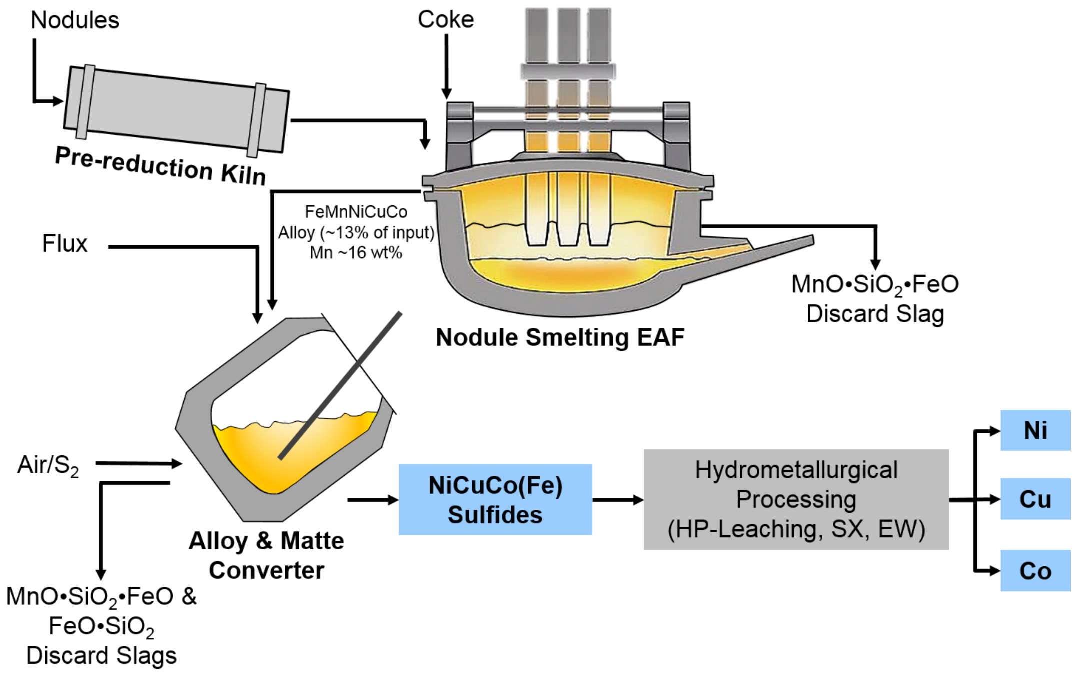

Figure 1: original OMI / INCO Process for Mn nodules (adapted from [7,8])

In this processing scheme, the nodules are fed wet into a gas- or oil-fired rotary kiln, in which drying and pre-reduction take place via a gas-solid reaction at approx. 800-900°C. By this carbothermic reaction Fe, Ni, Cu, Co are reduced to the metallic state. The charge is then fed into an electric arc furnace (EAF) and melted at 1450-1550°C. Thereby two main streams are produced; 13% form an iron-alloy and 81% are tapped as a manganese-ferrous slag. The use of the slag was hardly researched in the past and therefore the assumption was that this slag is dumped to a slagheap. About 6% of the Mn are co-reduced along with the valuable metals, whereby the alloy contains about 10-16 wt% Mn.

The goal for the nickel producer INCO was to obtain a known and by their operations treatable Ni-bearing stream. The high Cu and Co contents make a hydrometallurgical operation unavoidable. Thus, the alloy was converted to matte (sulfidic metal phase) after Mn and Fe are removed by converting with oxygen. This two-stage operation was carried out in a rotary converter with an oxygen-lance and the addition of elemental sulfur. This produces two additional slags and the Ni, Cu, Co containing matte. The matte may subsequently be pressure leached at 110°C with sulfuric acid (100 g/L H_2SO_4). The resulting leach solution is then treated in a multi-stage solvent extraction (SX) process to separate the three metals from each other. This liquid-liquid extraction process uses organic extraction-solutions specific to a target-metal to separate such chemically similar metals such as Ni, Cu and Co afterwards, the three metals can electro-won separately with high purity [7,8].

Optimized, zero-waste approach

In the past years, the institutes of Mineral Processing (AMR) and Process Metallurgy and Metal Recycling (IME) in close cooperation with the Federal Institute for Geosciences and Natural Resources of Germany (BGR) have developed an adapted and optimized metallurgical process for nodules with the goal “zero-waste”. Thus, manganese as a main product is considered much more intensely as it makes up more than 30 wt% of the nodules. Figure 2 shows a schematic flow chart for the process.

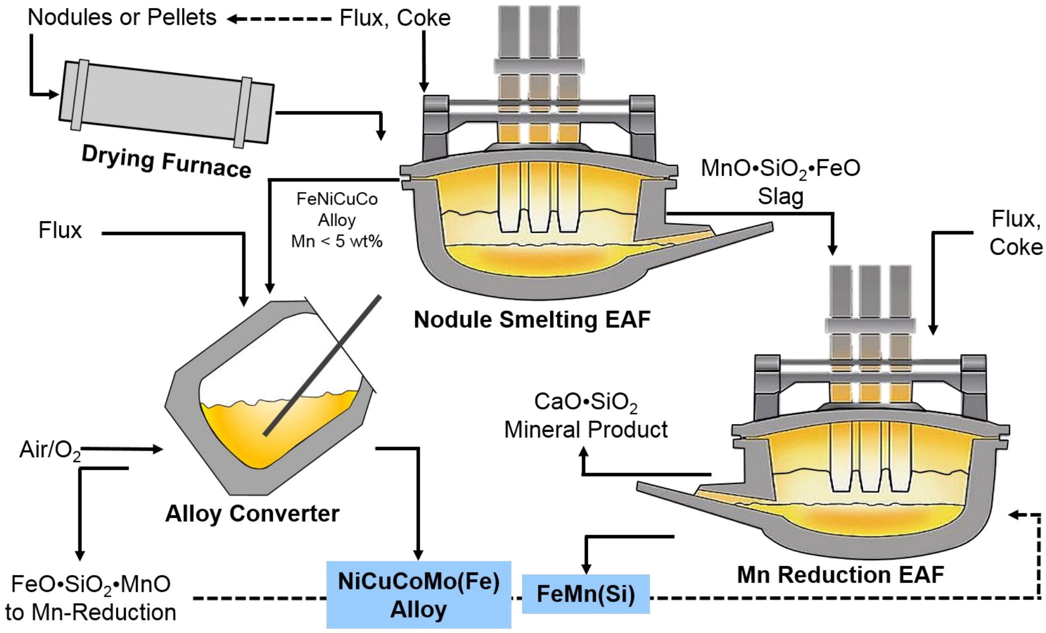

Figure 2: Optimized, zero-waste processing route for nodules [2]

Due to the high moisture and crystallization water contents of the nodules they need to be dried at 350-400°C before melting. A specific slag design through fluxing additives is proposed in the first melting step, whereby metal recoveries are increased while obtaining a more complete separation of the larger Mn-bearing stream (in the slag) from the metal stream (Fe alloy). The slag is then treated in another submerged electric arc furnace (SAF) to produce FeMn and a heavy-metal free slag that may be used as well. The details of this process optimization are discussed more closely in the following chapter.

THEORETICAL AND EXPERIMENTAL WORK

The above presented processing procedure was first evaluated theoretically and by thermochemical models in FactSage™ 7.0. Thus, processing windows were determined and later validated in lab-scale trials. Even though the databases in FactSage™ are not specifically tailored to the complex make-up of nodules, the models and experimental results are in good accordance. The pre-reduction step as in the original INCO process is deemed unnecessary from a thermodynamic perspective. During the pre-reduction in a rotary kiln, very small metallic particles are formed; this was demonstrated in a number of laboratory trials in a lab-scale kiln. However, during melting the metal particles quickly re-dissolve in the surrounding slag, since they are extremely fine-grained (<< 100 µm) and the slag/metal ratio is very high. Nonetheless, the nodules need to be dried at 350-400°C to remove their high moisture and crystallization water contents. Weight losses during drying are between 20-25%.

The first melting step is critical for an optimal processing scheme. Two simultaneous processes take place in the first melting SAF:

- Liquid slag formation
- Direct metal reduction from the liquid slag and metal phase formation

The relevant slag system in variation of the SiO_2-contents (i.e. MnO/SiO_2 ratio) is depicted in Figure 3 (FactSage™ databases FToxide, FactPS).

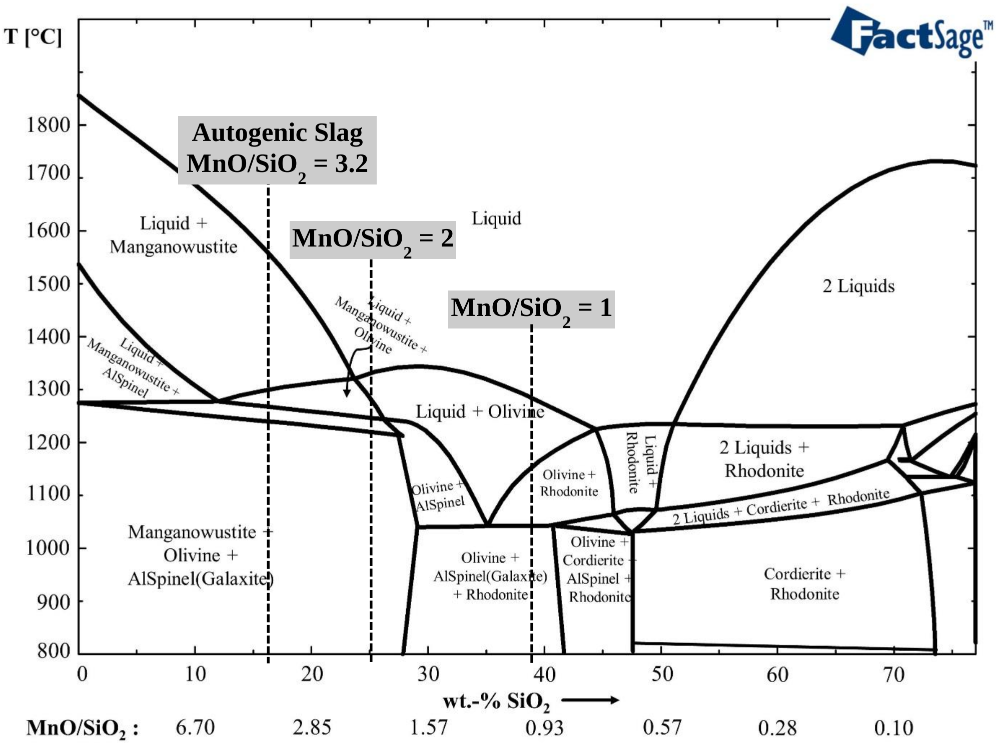

Figure 3: Quasi binary phase diagram of the five main oxides (MnO, SiO_2, FeO = 12 wt.-%, Al_2O_3 = 6 wt.-%, MgO = 5 wt.-%)

First melting and reduction furnace

Figure 3 shows that the autogenic slag formed by the nodules with no additives has a liquidus temperature of approx. 1560°C, which could be validated experimentally. This requires a processing temperature of above 1600°C (slag superheat) for the first reduction step. Above 1500°C MnO carbothermic reduction to metallic Mn is very significant, which is counterproductive to a complete Mn separation from the valuable metal constituents. Thus, the smelting and reduction temperature in the first SAF step needs to be reduced, thus a liquidus temperature set point < 1400°C was defined. Numerous flux additives were selected, modelled and tried experimentally. As Figure 3 shows, this goal is reached at best by an addition of silica flux. The MnO/SiO_2 ratio proved a reliable parameter for good process control. [1]

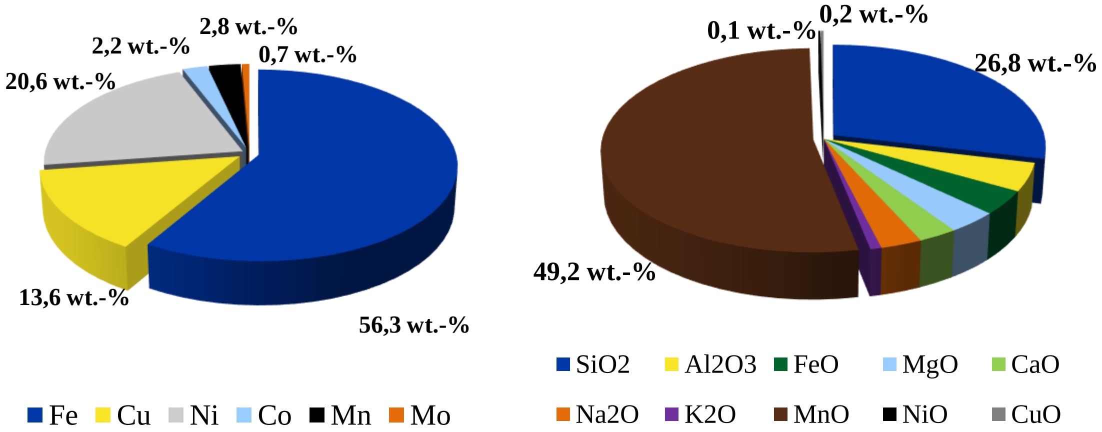

Figure 4: Average alloy (left) and slag (right) composition after first reduction step for $MnO/SiO_2 = 2$ [1]

The averagely obtained metal and slag compositions are shown in Figure 4. All trials were carried out in a lab-scale electric arc furnace. High recovery rate for the valuable metals > 90% are generally proven. Cu losses in the slag remain somewhat high and will be investigated further. The optimized first reduction step yields concentration factors for Ni, Cu, Mo and Co > 10, which could never be reproduced via beneficiation methods. The high MnO containing slag is subsequently used for FeMn recovery, which is discussed in the following chapter.

Ferro-manganese recovery in second reduction furnace

For the reduction of ferromanganese a slag with 47.4 wt.-% MnO was generated from a larger trail series with an adjusted MnO/SiO_2 ratio of 2 in the first melting and reduction step. A value for the basicity was established to describe the reduction step:

$$B = \frac{\%MnO + \%CaO}{\%SiO_2} \quad (1)$$

The autogenic slag possesses a basicity value of 1.63. This highlights the challenge for the FeMn reduction from this slag, when compared to standard manganese ores; whereas the Mn content of the slag is comparable to manganese ores , the basicity (i.e. silica content) of the slag is significantly higher (i.e. more acidic; B = 3…17) [2]). Thereof arises the need for CaO flux to hold Si in the slag. The trial results are illustrated in Figure 5. The basicity was increased (2.4, 2.6, 2.8 and 3.0) for these trial series. As can be seen from Figure 5 the lowest Mn content in the final slag may be achieved with the highest CaO additions.

The resulting FeMn metal phases showed a manganese content of > 85 wt% in XRF analysis. Fe content in the alloy is ~ 8 wt%, which is inside requirements for FeMn. Yet, titanium as well as vanadium content in the reduced metal is problematic with contents ~ 1.3 wt% and 0.4 wt%, respectively. The control of these metals will be subject to further studies. The phosphorous contents on the other hand was not significant and below 0.1 wt.-%. Reduction temperature during holding varied between 1600 and 1800°C as was calculated in the simulations.

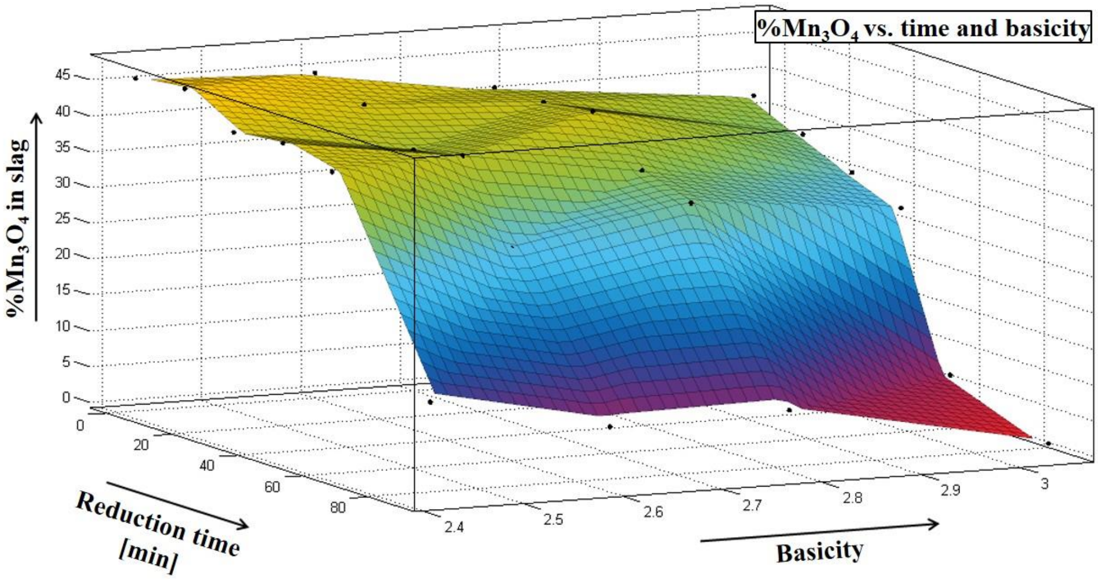

Figure 5. Correlation of Mn content in the slag during reduction versus holding time and basicity

Keywords: Direct slag reduction, Polymetallic deep-sea nodules, Pyrometallurgical treatment, Zero-waste processing, Submerged Arc Furnace (SAF)

David Friedmann

David Friedmann began his studies in 2008 at RWTH Aachen University. In 2011 he received a Bachelor of Science degree. In 2014 he graduated with a Master's degree in metallurgical engineering. Subsequently he started his PhD assistant's job in 2014 at IME, department of Process Metallurgy and Metal Recycling, focusing on the metallurgical treatment of deep-sea minerals. Special focus here lies on the zero-waste processing of polymetallic manganese nodules as an alternative mineral resource for Nickel, Copper, Cobalt, Molybdenum and Manganese.

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