PROGRESS IN RECYCLING SLUDGE FROM OFF-GAS CLEANING OF MANGANESE ALLOY FURNACES

[1]B. Ravary, [2]L. Hunsbedt, [3]O. Kristensen

[1] Eramet Norway AS, Alfred Getz vei 2, 7465 Trondheim, Norway
benjamin.ravary@erametgroup.com
[2] Eramet Norway Kvinesdal AS, 4484 Øyestranda, Norway, leif.hunsbedt@erametgroup.com
[3] Kristensen Consulting Norway AS, Risløkkveien 25 D, 0580 Oslo, olav.kristensen@vikenfiber.no

ABSTRACT

Cleaning of off-gas using wet scrubber generates sludge from dust and condensable species. This sludge concentrates a number of problematic elements, in particular tars, heavy metals and alkalis. Recycling into conventional Submerged Arc Furnaces (SAF) may be possible after some treatment of the sludge. Treatment is needed to remove elements that can be detrimental to the production efficiency and safety. Eramet Norway has more specifically investigated the feasibility of melting the sludge to either produce a slag for recycling in SAF and a cast metal, or directly a metal, using an open bath electric arc furnace.

The main process areas are the preparation of the sludge (dewatering, drying, possibly calcining), the melting (with associated casting and handling of the products) and the off-gas treatment. The current paper describes the main characteristics of the sludge (physical and chemical) and recent developments in finding industrial solutions for the drying.

KEYWORDS: *Manganese, environment, sludge, valorization, recycling, characterization.*

1. INTRODUCTION

Sustainable manganese alloy production is a goal for the industry. Important aspects to reach this goal include the maximum use of the valuable elements in the raw materials and minimum emission to the environment.

The production of manganese alloys in Submerged Arc Furnaces (SAF) has as major by-products slag from SiMn production and dust carried away with the off-gas. The off-gas cleaning of closed furnaces in Norway (figure 1) includes wet scrubbing. The sprayed water collects most of the dust. The polluted water goes through a thickener. The underflow from the thickener is de-watered mechanically to produce sludge. This sludge is currently sent to landfills.

A previous publication [1] provided a short literature review on manganese sludge treatment. It is not repeated here. It also presented some main characteristics of the sludge, based on a weighted average on Norwegian plants.

The main characteristics of the sludge were: high water content, above 50 %, fine particulate (d_{50} between 1 and 4 μm), carbon content around 10 %, and presence of alkalis, Zn, Pb and other heavy metals.

Finally, based on analysis of several possible treatment options as well as some test work at laboratory and small scale pilot experiment, it recommended a smelting before recycling into SAF. This was the only way identified at the time to remove both alkalis and Zn and Pb, which are unwanted elements back to the SAF.

The current paper will present some progress on the path of finding a sustainable solution for treating the sludge.

2. CHARACTERIZATION

The chemical composition of sludge varies over time, depending on the raw materials and the conditions in the furnace. It is therefore difficult to capture a representative sludge. Tests have been performed on various sludges over the last three years.

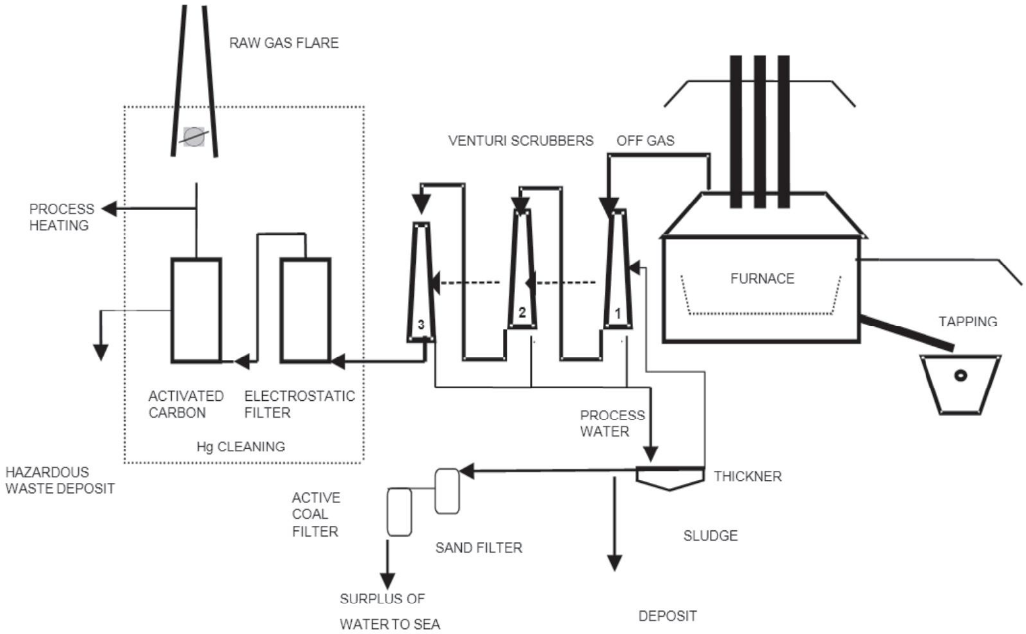

Figure 1: Gas cleaning system of SAF

2.1. Distribution between inorganic and organic carbon

In order to develop treatment options as well as understanding what kind of reactions are to be expected under different conditions, it is important to find out in what form the carbon in the sludge is present. The carbon present in the sludge comes originally from the volatiles present in the raw materials, some coke breeze carried away by the off-gas flow and possibly carbonates present in fine raw materials. Quenching and chemical reactions in the scrubbers will generate different carbonaceous molecules that are found in the sludge.

Samples from both SiMn and FeMn production from Eramet Norway's three plants have been taken over three days in January 2011. These samples have been analyzed for Total Carbon (TC), Inorganic Carbon (IC) and Organic Carbon (OC). These analyses were performed at Centre Terre et Pierre (CTP) in Belgium. For the total carbon content, the sample is calcinated at 900°C. The carbon dioxide formed during the pyrolysis (after combustion) is analyzed and quantified by infrared light. For the inorganic carbon determination, the sample is treated by phosphoric acid at 200°C. Again the carbon dioxide formed is analyzed and quantified by infrared light. The organic carbon is obtained by difference.

Some results of the analyses of dried sludge are presented in table 1. The amount of carbon is significantly lower than the results presented in [2] for TEMCO operation, for which C content was up to 21.8 %.

The present results and historical results not presented here indicate generally higher total carbon content for HC FeMn than for SiMn production. There are many parameters varying between these two types of production so an attempt to explain this difference would require a comprehensive analysis. The temperature in SAF is generally higher in SiMn furnaces than in HC FeMn. The specific dry sludge production per ton metal is significantly higher for SiMn compared to HC FeMn, as higher temperature for similar furnace areas will give higher gas velocities and more entrainment of particles. This is confirmed by the diameter of the sludge particles in SiMn which is larger than for HC FeMn. Assuming that fine reductant particle entrainment will vary similarly as other particles, the difference may come from the volatiles. Pyrolysis varies with temperature. At constant or little varying evolution of volatiles, the carbon content will be less simply by greater dilution with more non carbonaceous materials for SiMn.

Table 1: Carbon in different sludge , wt%

	TC	IC	OC	IC (% of TC)
HC FeMn - plant 1 - sample 1	13.2	7.3	5.9	55%
HC FeMn - plant 1 - sample 2	12.1	8.6	3.4	72%
SiMn - plant 2 - sample 1	4.6	3.2	1.5	68%
SiMn - plant 2 - sample 2	5.5	3.8	1.6	70%
SiMn - plant 2 - sample 3	4.9	3.7	1.3	74%
SiMn - plant 3 - sample 1	7.7	3.5	4.2	46%
SiMn - plant 3 - sample 2	9.3	3.6	5.7	39%
SiMn - plant 3 - sample 3	9.3	3.9	5.4	42%

In the samples analyzed, the proportion of inorganic carbon varies between 39 % and 74 %. This proportion can be both lower and higher for SiMn sludge compared to HC FeMn.

2.2. Mineralogy

Samples of dried sludge have been investigated by X-Ray Diffractometry (XRD) to determine the mineralogy. Two research laboratories were used by Eramet Norway, using the material from the same samples. Results obtained by the two teams were similar, with minor variations for species in low concentration, probably due to the equipment and analysis software used.

XRD can well analyze crystalline phases while amorphous phases cannot be analyzed with this technique. FeMn sludge was mostly crystalline while SiMn sludge contained a large proportion of amorphous phases. This difference may be due to the difference of conditions in the two types of furnaces, as well as the fact that for SiMn, quartz was entrained and silica is semi-amorphous.

For all sludges, the dominating crystalline phase was rhodochrosite $MnCO_3$.

This phase was very dominating for FeMn sludge (which has again a high crystallinity). One research laboratory identified manganosite MnO with graphite C in the sample from one plant and manganosite MnO and hausmannite Mn_3O_4 in the sample from another plant, as being other phases in traces. For this last sample, the other research laboratory found the following phases in addition to manganosite (in order of decreasing amount): dolomite $CaMg(CO_3)_2$, zincite ZnO and smithsonite $ZnCO_3$, kutnohorite Ca(Mn,Mg,Fe++)$(CO_3)_2$ and calcite $CaCO_3$.

SiMn contained a relatively large amount of amorphous phases. For both XRD analyzes, the crystalline phase included mainly rhodochrosite $MnCO_3$, dolomite $CaMg(CO_3)_2$, quartz SiO_2 (semi-amorphous) and calcite $CaCO_3$. One research laboratory further identified kutnohorite Ca(Mn,Mg,Fe++)$(CO_3)_2$. The other laboratory found instead graphite C and hematite Fe_2O_3.

The authors of the current paper are not expert in XRD analyzes and therefore cannot discuss the differences in interpreting the XRD results by the two research laboratories. The main phases were similar and in line with previous measurements performed in [2]. For the development of a treatment option, determining the phases for alkalis Zn, Pb and other heavy metals was particularly interesting. One laboratory claims finding Zn phases while the other one could not, as in [2]. The low concentrations of these elements seem to make XRD not adapted. Scanning Electron Microscopy (SEM) combined with Electron Probe Micro-Analysis (EPMA) could provide more information.

It is also interesting to find out how the phases are distributed in space in order to understand if some of them can be separated by mechanical means. Shen et al. [2] found by EPMA that Zn was uniformly distributed.

3. DRYING TEST WORK

Test work at different scales up to semi-industrial has been performed, in order to find out equipment and technology for different treatment options or sub-processes. Here we will only review briefly test work performed to qualify drying equipment.

The sludge before drying is difficult to handle and feed into any equipment. This has been an important challenge in all the test work. In several cases, we had to feed manually the sludge since the feeding system that was mounted on the test equipment was not adapted. Feeding equipment should be focused on in future development work, in cooperation with vendors.

Several equipment may be used for drying. The following equipment have been tested during the current development work: flash drier, rotary kiln and high intensity mixer.

Flash drier made it possible to effectively decrease the moisture below 2 %, without any issue for the equipment. No build up was observed. In the test equipment, we could reach a feed capacity of 240 kg/h and an inlet temperature of approximately 640°C was used.

1m-diameter and 6m-long rotary kiln using indirect electric heating has been tested. The sludge rheology made feeding very difficult. By mixing some wet and dried sludge together, the feeding was somehow easier but there were still problems. Agglomeration happened, giving large granules or pellets of varying size depending on operating conditions. By heating at 160°C for approximately 1.5 h, the product obtained had lost half of its initial water content and consisted of a mix of pellets and powder.

A laboratory scale high intensity mixer with electric heating elements in the walls has been used for drying and pelletizing at the same time. Six batches of 2-3 kg were treated showing the ability of the equipment to produce small pellets (0.5 mm diameter) that could further be handled easily. Larger test work is needed to further confirm these promising results.

4. CONCLUSION

Progress to develop a treatment route for sludge from off-gas cleaning system of manganese alloy SAF is presented. The chemical composition and the phases present in the dust have been investigated. A large proportion of the carbon in the dried sludge is inorganic. Carbonates are dominating phases, in particular manganese carbonates, rhodochrosite.

In the path of developing an industrial treatment, several test works were carried out. They showed that feeding the sludge was particularly challenging and should be further worked on. Several drying techniques have proved effective though techno-economic studies. Further work is needed to conclude the most economic and hence efficient to the downstream processes.

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