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# Oxidative leaching of a sulfidic flue dust of former copper shale processing with focus on rhenium

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ABSTRACT

The investigation aims at a hydrometallurgical processing approach for an environmentally hazardous material called “Theisenschlamm”, which is a flue dust of former copper shale processing in Germany. Besides eliminating the negative environmental impact, processing of this material would also be a contribution to a circular economy, since it contains about 16 wt.-% zinc, 14 wt.-% lead, minor amounts of copper and tin, as well as valuable elements of strategic economic importance, such as rhenium, molybdenum and germanium. The mainly sulfidic matrix of the Theisenschlamm was characterised using scanning electron microscopy in combination with QEMSCAN software. Leaching of Theisenschlamm in acidic and alkaline media, as well as the effect of oxidising agents, was studied in order to extract zinc, copper, rhenium, germanium and molybdenum. In both sulphuric acid and sodium hydroxide solutions, the addition of oxidising agents (hydrogen peroxide and ozone) improved metal extraction efficiencies significantly. The leaching system sulphuric acid/hydrogen peroxide was investigated in more detail, with focus on the optimisation of rhenium extraction and its effect on the extraction efficiencies of the other target elements. Response surface methodology was applied with respect to $H_2SO_4$ concentration (0.1–1.2 mol/L), $H_2O_2$ concentration (0.1–2.8 mol/L) and solid:liquid ratio (40–150 g/L). This study shows that oxidative leaching enables the extraction of zinc, copper, rhenium, germanium and molybdenum from this sulfidic material. In terms of rhenium extraction, a low acid concentration is favourable; however, lowering the acid concentration results in a reduced yield of other target elements (e.g. molybdenum).

## 1. Introduction

Metals such as rhenium, molybdenum or germanium are becoming more and more important in modern high-tech applications. Highly efficient turbines could not be realised without rhenium, since this metal increases creep strength of nickel-based superalloys (Polyak, 2015). Molybdenum is also of great importance in the production of alloys, as it improves strength as well as resistance to corrosion and heat (Shields, 2013). Due to its optical properties, germanium is indispensable in modern communication technologies (e.g. optical fibres), and is furthermore crucial for infrared optical equipment (Marscheider-Weidemann et al., 2016). Theisenschlamm (English: Theisen sludge), a flue dust of the former copper shale processing in the Mansfeld region in Germany, is a potential resource for these important technology metals, and others including zinc, lead and tin. Until 1978 the sludge was processed in a lead shaft furnace because of its high zinc and lead concentrations. After closing down the lead smelter, a total of 220,000 tons of Theisenschlamm had to be dumped until copper shale processing was stopped in 1990 (Daus and Weiss, 2001). Besides its valuable metal content, further characteristics of Theisenschlamm are very fine-grained particle size, and a high organic content of about 10% compounds such as polycyclic aromatic hydrocarbons and polychlorinated dibenzodioxins/-furans (Weiss et al., 1997). Theisenschlamm also emits alpha-radiation of 9.15 Bq/g (measured in 2015), which is mainly caused by the isotope $^{210}$Pb. These properties highlight the potential of this material to cause a negative environmental impact. It is stored in a covered waste dump; however, contamination of the environment cannot be ruled out. Thus, the challenging goal of this

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work is to eliminate such pollution by processing the material, recovering the valuable elements, and producing a residue that can then be used in applications such as road construction or concrete production. Besides the environmental aspect, making these elements available on the market would also be a contribution towards establishing a circular economy (European Commission, 2014).

Processing of Theisenschlamm has already been considered by several approaches, with focus on different target elements. In the 1980‘s investigations using a flash furnace revealed that only enrichment of the metals was possible, but no selective extraction since scattering of the metals between an oxide and a sulphide phase as well as polymetallic flue dusts occurred. Thermodynamic considerations by Leipner et al. (1991) showed that melting processes to produce lead and zinc, such as top blown rotary converter (TBRC), Queneau-Schuhmann-Lurgi (QSL) reactor or flash furnace are not suitable, since the activity of lead oxide is decreased in the slag. Consequently, higher process temperatures are required to convert lead sulphide to elemental lead, instead of forming lead oxide. As a result of the higher temperatures, which lead to increased vaporisation, loss of lead occurs.

Oxidative roasting of Theisenschlamm was suggested as a pyrometallurgical alternative. It was determined that mainly lead sulphate as well as zinc silicate ($Zn_2SiO_4$) are formed by roasting with air at 750 °C, and that the carbon content can be reduced to < 0.1%. The roasting product could be used as feed in an imperial smelting (IS) furnace (Leipner et al., 1991). This approach was further investigated by the former Lurgi AG together with the Mansfeld AG. A concept including exploitation, processing and roasting was developed (Lorenz et al., 1992). Drawbacks of this approach are that the roasting process requires several preparatory steps and a comprehensive off-gas cleaning system. No information about the low-concentrated elements, such as rhenium, was reported.

These previous investigations reveal that a roasting process alone could only serve as a pre-treatment, but requires complex equipment. Selectivity issues were reported for melting processes. Nevertheless, the formation of a dense slag is advantageous, since it provides a better structure for road constructions, for example, when compared to fine-grained leaching residues. Therefore, investigations with versatile aggregates, such as the top submerged lance (TSL) reactor (Outotec, 2018), could be considered. Furthermore, the distribution of not only the main elements but also of low concentrated elements (e.g. rhenium oxides in the gas phase) would need to be determined. Due to a high lead content of about 14 wt.-%, Theisenschlamm could be a possible feed material in lead pyrometallurgy like in the former copper shale process. The literature shows that reactors such as the TSL can process a variety of materials by adjusting a specific feed composition (return slag, additives e.g. calcium oxide etc.), gas atmosphere and gas flow, as well as application of multi stage processing which includes recycling of flue dusts and other outputs (Kaye et al., 2008; Helin et al., 2012). It is therefore assumed that Theisenschlamm could also be a possible feed in those processes. Van Schalkwyk et al. (2018) summarised the complexity of element distribution and challenges in lead pyrometallurgy, explaining the necessary considerations for developing and optimising future-oriented metallurgical processes in a circular economy.

Different leaching processes have been investigated to treat Theisenschlamm with hydrometallurgical methods. Table 1 gives an overview on the leaching yields of the elements of interest in those processes. Oxidising pressure leaching in sulphuric acid under application of 10 bar oxygen pressure and a temperature of 170 °C showed high yields of rhenium, as well as zinc and copper. As was intended, lead remains in the leaching residue. Since the organic content in Theisenschlamm is high, a continuous exchange of the gas atmosphere was necessary to avoid breakdown of the oxidation reaction caused by high carbon dioxide concentrations. Further improvement of the leaching yields could be achieved by chemical, thermal or mechanical pre-treatment of Theisenschlamm, (Reiss and Gock, 2015) but high pressure and temperature are needed, and special process equipment is required, all of which increases process costs. Morency et al. (1998) suggested another hydrometallurgical process, called Theisenschlamm oxidation process (TSOP). After grinding and drying, the material was leached with a 30% hydrogen peroxide solution. This investigation revealed yields higher than 90% for rhenium, copper and zinc (Weiss and Morency, 1997). The main disadvantage of the TSOP is the very high hydrogen peroxide consumption, and consequently high operation costs. Bioleaching was considered as a cost- and resource-efficient method to extract the valuable metals from Theisenschlamm. Yields of zinc, copper, and especially rhenium, are lower than with the aforementioned chemical leaching methods (Klink et al., 2016). High yields of the heavy metal content are not only beneficial regarding economic viability, but also for obtaining a residue that can be processed to further products. Moreover, leaching durations of more than 20 days show that the kinetics of the bio-hydrometallurgical process are slow, limiting the economic feasibility. Leipner et al. and Lorenz et al. mentioned a different pressure leaching approach in alkaline media. Although it resulted in good rhenium as well as selenium and molybdenum extraction, zinc and lead could not be separated and the method was not economical (Leipner et al., 1991; Lorenz et al., 1992).

**Table 1**
Metal extraction of previous leaching investigations (in %).

| Elements | Zn | Cu | Re | Ge | Mo | Pb | Ref. |
|---|---|---|---|---|---|---|---|
| Pressure leaching[a] | 92 | 75 | 67 | n/s | n/s | 0 | (Reiss and Gock, 2015) |
| TSOP | 94 | 93 | 91 | 40 | 0 | 0 | (Morency et al., 1998) |
| Bioleaching | 70 | 45 | 20 | n/s | n/s[b] | n/s[b] | (Klink et al., 2016) |

n/s: not specified.
[a] Values estimated from diagram data.
[b] Concentrations in pregnant leach solutions are very low compared to other elements (e.g. zinc).

Hydrometallurgical treatment showed that separation of the main elements (e.g. zinc and lead) can be achieved. Since the variety of hydrometallurgical separation and enrichment processes would allow a flexible process design to recover the low-concentrated strategic elements (e.g. rhenium or germanium), a hydrometallurgical process route seems to be a promising approach for Theisenschlamm treatment. The idea is to apply only as many process steps as necessary to either produce marketable products, or form intermediate products which can be fed into existing processes (e.g. zinc or copper metallurgy). A residue that can be further used, for example as building materials, should be obtained. Thus, this study deals with the first process step (leaching of Theisenschlamm under ambient pressure, low temperature and optimised consumption of chemicals such as the oxidising agent). The aim is to recover zinc and copper as well as rhenium and other low-concentrated elements such as molybdenum and germanium. Optimisation of the leaching conditions is focussed on rhenium. The elements lead and tin should be concentrated in the leaching residue in order to be separated and recovered in another process step, which will produce further products and building materials.

This purely hydrometallurgical approach is a first step in developing a new flowsheet to process complex materials such as Theisenschlamm. A comparison or combination with pyrometallurgical methods, such as a TSL reactor, should also be considered since these processes show good possibilities to minimise residues by producing slags for use as building materials. In the development of innovative metallurgical processes both options, and their combinations, must be taken into account. As an example, this was discussed by Reuter and van Schaik (2016) for gold recycling from waste electric and electronic equipment. The economics will dictate what process flowsheet is best i.e. which combination of hydro- and pyro-metallurgical processing will best recover all elements economically while producing building materials and final residues which can be deposited for further processing in future, when the economics render this possible. An overview of future challenges in process metallurgy and its role in realising the circular economy is also given by Reuter (2016).