

## 10. Feasibility Study of the Treatment for Theisenschlamm with Hydrogen Peroxide

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### Abstract

The treatment of Theisenschlamm with hydrogen peroxide, was developed in the laboratory as a batch process and at this stage, no attempt was made to upscale the process. The technique has produced excellent results regarding the elimination of organic compounds, separating and recovering the main components lead and zinc. In so doing, the associated radiation is now concentrated with the lead phase. The phase transformation and the resulting separation allow for the recycling of zinc, lead and other valuable metals and at the same time eliminates the environmental problems inherent with the Theisenschlamm. Unlike disposal, this procedure could be a final solution to the problem. The cost associated with the treatment is offset by the value associated with the recoverable metals. The feasibility study presented in this paper considered the process as an industrial continuous treatment process. The process can also be designed to be applied to other environmental problems in particular those related with sulphide residues from mining activities.

### Options considered for solving the Theisenschlamm problems

Due to market globalisation and a greater accessibility to raw materials markets, Theisenschlamm is only of limited interest as a source of raw material (Steinkamm 1994). This explains why disposal is being considered as the main option.

In addition, the amount of chemical elements which are banned or restricted like thallium and mercury is small, less than 100 tonnes which means that expenditure for proper storage would be low. However other more serious problems would arise in connection with cell storage owing to the amount of arsenic (some 1,430 t) in the sludge. Also, depending on the method used, other residues will result which would in turn require storage or management of these residues.

According to KRAMM (1994), there are three viable options for the safe storage of Theisenschlamm:

- Local safeguarding

- Disposal elsewhere above ground
- Underground storage in mine galleries

Option 1 is associated with the risk of sink holes. Option 2 would be subject to constant aftercare costs. The drawback of Option 3, the safest approach, is that it impedes subsequent treatment and the associated cost is high. These options do not offer a permanent solution and no return or cost reduction from added value from recycling is possible.

When it originally arose, the Theisenschlamm problem was less serious, but with time alterations through oxidation with the help of microorganisms brought about the generation of acid water with the resulting metal dispersion in the environment. These microorganisms, including those which could very well carry out the conversion of sulphides and organic compounds (STOLL, 1994) are presently at work except that this process is not controlled and will take several decades or centuries for complete restoration.

Hence dumping will not solve the problem in the long term, but will simply pass on the responsibility to subsequent generations. Dumping should only be regarded as an emergency solution in the absence of proper treatment or recycling methods for the Theisenschlamm.

The following possibilities were suggested for treatment:

- Physical separation
  - Colloidal separation (MORENCY, 1994)
  - Wet magnetic separation (MORENCY, 1994)
- Hydrometallurgical separation techniques, e.g.
  - VITROKELE methods with prior extraction of the organic components (Gesellschaft für Beseitigung und Sanierung von Altlasten mbH, 1994)
  - Sulphuric acid oxidising pressure leaching (GOCK & SÖTEMANN, 1994)
- Pyrometallic separation techniques, e.g. calcination (LURGI method) with post-combustion and purification of the calcination gas (WEILANDT, 1994)
- Microbiological techniques, e.g. using 'chemolithotrophic' bacteria (STOLL, 1994)

Other processes are described and assessed in LORENZ (1994), STEINKAMM (1994) and LEIPNER (1994). However, none of these methods provide a satisfactory solution to the Theisenschlamm problems.

The proposed oxidation process using peroxide treatment is a possible permanent solution which recovers valuable metals from the Theisenschlamm for further processing. This approach is in stride with the concept of industrial ecology.



## Description of the reaction process

The method comprises directly mixing the Theisenschlamm with an  $\text{H}_2\text{O}_2$  solution. The laboratory-scale experiments are described in Chapter 9. An exothermic reaction with a sharp rise in temperature occurs, which must be taken into account when designing the industrial plant.

A liquid and a solid phase are produced, which are separated by filtration. The sulphation (oxidation of the sulphidic components) results in the very good separation of lead and zinc. The organic substances are almost completely destroyed in the solid residue and only small amounts are present in the liquid phase (see also Chapter 9). For our purpose the initial and final state of these organic substances will not be considered any further in this paper.

The results of the laboratory batch experiment displayed an abrupt transition from the normal, slow oxidation reactions to spontaneous reactions that cannot be controlled on a batch industrial scale. In the laboratory, it was also established that the reaction could be initiated and would still result in a non-controlled exothermic reaction for concentration of  $\text{H}_2\text{O}_2$  as low as 3%. Therefore one of the goal of this feasibility study was to evaluate if the process can be converted to a continuous process.

## Description of the thre phases involved with the reaction

- *Gas phase*

During the reaction, carbon dioxide is released by the destruction of organic substances resulting from the oxidation of carbon, this is also accompanied by the emanation of steam. Since these experiments were carried in open vessels, and the gas phase was not collected for detailed quantitative analysis, undoubtedly, other decomposition products such as carbon monoxide, oxygen and hydrogen are certainly present. However, the process can be designed such that the amount of steam is minimised in order to avoid large heat lost. Moreover, process management must also take into account the fact that this gas development is accompanied by the formation of foam, and therefore a sprinkling system combined with cooling are required.

- *Liquid phase*

The liquid phase turns out, after filtration, to be a clear liquid mainly containing zinc sulphate. However, the zinc concentration is not very high, owing to the process involving high excess  $\text{H}_2\text{O}_2$ . The dilution lowers the zinc content from an average of 18% in the original solid to about 7.5% in solution, nevertheless a local electro-chemical treatment and metal extraction could be feasible.

- *Solid phase*

In the solid phase, the lead sulphate is enriched which in turns increases the radioactivity of the material. Although  $^{210}\text{Pb}$  is dangerous in the form of very fine distributed particulate as it can penetrate the respiratory system of the human body, causing radioactive harm. The same material is harmless once process into lead products like bricks or batteries for motor vehicles. The type of radiation associated with  $^{210}\text{Pb}$  only travels a few centimetres in air. Therefore this type of lead can be used safely with industrial products. The lead concentrate could be used at a smelting plant (Gesellschaft für Beseitigung und Sanierung von Altlasten mbH, 1994). Moreover, LEHMANN (1994) draws attention to the fact that the radioactive hazard of the lead present is outweighed by its chemical hazard. Therefore, when treating Theisenschlamm, special radiation protection measures are not required but the dust from a dried slurry can be a serious problem if inhaled.

### **Reaction parameters**

This type of reaction responds to different kind of parameters and in our laboratory study, these parameters have hardly been studied in particular with respect to continuous process control. Therefore, only general remarks can be made at this time. Grain size, ratio of solid:liquid, pH-Eh and residence time for a complete reaction are required for the upscaling to a full-scale industrial plant.

- *Temperature influence*

Any increase in temperature has a positive effect, for example by significantly reducing the reaction times.

The course of the reaction indicates that if the components are pre-heated (e.g. to  $55^{\circ}\text{C}$ ), the long initial waiting phase can be reduce considerably and the oxidation process should begin shortly thereafter with the oxidation and destruction of the organic compounds. The subsequent sulphide oxidation could take place earlier and attain a higher temperature if prior destruction of bituminous particles and organic coating of the feedstock has been accomplished.

This temperature pre-treatment is limited by the dissociation possibility of the  $\text{H}_2\text{O}_2$  and the greater steam generation in the gas phase. Evaporation/sublimation from the Theisenschlamm is not expected below  $100^{\circ}\text{C}$ .

- *Pressure influence*

Increasing the pressure is not expected to change the reactions in the liquid phase and so the process can be carried out in the atmospheric range. This is convenient for the plant design.



- Treating other substances

The high energy gain would allow other substances to be treated simultaneously, as long as this does not impair the reaction mechanism. At the moment, suitable substances include neutral or sulphurous wastewater (as sulphide, sulphite or sulphate), sludge containing heavy metals, organic impurities (anode sludge), fly ash and residual materials from smelting plants in the region (WEILANDT, 1994). On the other hand, processing waste containing  $\text{NO}_x$  or halogens depends on the quality of the subsequent waste gas scrubbing system and this may render the material selection difficult.

### Principles related to an industrial process design

Theisenschlamm cannot be directly recycled regardless of the methods used, its complexity make it impossible to obtain directly recyclable products in a single stage process. Ultimately hydrogen peroxide treatment results in products (e.g. zinc as sulphate in the liquid phase, lead as sulphate in the solid phase), which can be easily processed in other useful products. The spontaneous reactions during the discontinuous process show that the method can only be controlled if conducted in a continuous process with the liquid phase.

Slurrying the Theisenschlamm is a stage which would also have to take into account the impurities mixed within the slurry. In addition a separation stage (filtration) for the solid-liquid recovery when the reaction is completed will also be required.

Post-treatment is essential for the gas, liquid and solid phases. Impurities or other rejects from the process have to be kept to a minimum. The estimate made by WEILANDT (1994) that 5–6% of the Theisenschlamm will need to be disposed of may well prove to be excessive.

The main process flow should be carried out using an 'online' technology. Conducting the  $\text{H}_2\text{O}_2$  reaction stage as a two-stage reaction appears suitable. The heat from the reaction (exothermic) should be dissipated via a closed cooling system (hot-water system) to which heat consumers are connected directly or indirectly assuming the heat can be sold. The system should contain emergency coolers and an emergency heating boiler. The heat exchangers could also, if necessary, function not only as coolers but also as pre-heaters during start-up processes and pre-treatment of the slurry.

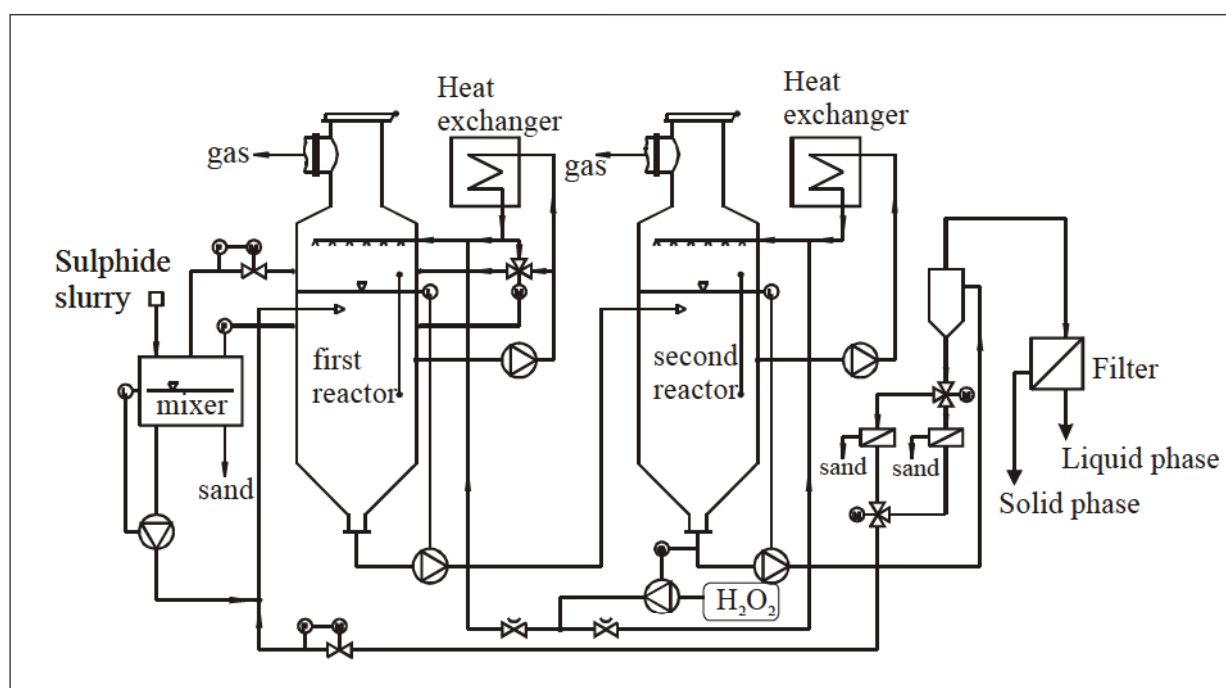
In all other respects, the method is subject to the same principles and conditions that guides the operation of a standard chemical plant (i.e. safety, environmental protection, etc.).

### Flow process for an industrial production plant

The industrial process is centered around the reactor and is characterised by the following associated stages:

- Pre-treatment of the starting materials;
- Introduction (dosing) of the starting materials;
- Reaction per se;
- Output of intermediate products;
- Output of final products;
- Separation of final products.

The Theisenschlamm must be kept in suspension while undergoing this wet oxidation treatment. This can be carried out with a hot process solution in a mixer (see Figure 1). The coarse natural components (coarse gravel, sand, and slag) must also be removed in this mixer otherwise they could disrupt the flow process and the re-circulation and cooling processes.



**Figure 1:** Flowsheet of the process

Of course, the Theisenschlamm must initially be collected, transported, placed in a silo for interim storage in a state suitable for a slurry preparation. The Theisenschlamm in a slurry form, will be pump and injected via a nozzle into the primary reactor, where already turbulence and mixing are ongoing due to the violent reaction.

The primary reactor should be cooled by an unregulated circulation pump with a subsequent hot-water cooler. Temperature control (not shown) will take place on the hot-water side depending on the amount of cooling water required. Shortly before entering the sprinkler system, the hydrogen peroxide solution is added. Sprinkling will destroy the foam created during gas development and will also cool the system.

As already mentioned above, the main purpose of the first reactor is for the breakdown and destruction of the organic substances. Therefore, considerable gas and steam formation will take place in this reactor, and the sprinkling capacity should be designed accordingly.

After a certain residence time in the first reactor and depending on the level of the material, the content is pumped into the second reactor. The procedure in this reactor is identical to the first one .

A cyclone is used after the second reactor to separate coarse material from the fine components. A partial flow is returned to the first reactor via the sand filters. Two sand filters are used in order to allow for cake recovery which can accumulate after several cycles of processing. The recovered sandy material is washed, flushed, and if necessary screened to provide a usable building or filling material. The fine-grained water–solid mixture from the cyclone is separated on the filter. Experiments must be conducted to select the type of filter most suited for the process. Although all the process stages need to be tested, they can all be controlled with the current engineering state of the art and the process can be implemented on an industrial plant. The reactor material would need to be enamelled in order to provide resistance against acid components and corrosion. Austenitic steels, e.g. V4A, or steels such as that employed in flue gas scrubbing plants containing  $\text{SO}_2$  should be used for pipes, fittings and the heat exchangers (conventional plate exchangers). Stainless steel, ceramic materials (porcelain) or steel with mineral coating (enamel) would be suitable. Polytetrafluoroethylene (PTFE) could be used as a sealing material.

The control equipment for the plant comprises relatively simple temperature gauges, level monitoring and throughput controls. The pumps should preferably feature speed control using frequency converters. Hydrogen peroxide solution should be fed at a rate which depends on the residual concentration of  $\text{H}_2\text{O}_2$  and free oxygen measured at the reactor output.

As far as safety is concerned, care should be taken that the amount of  $\text{H}_2\text{O}_2$  added to the first reactor does not exceed the required amount which is actually consumed for the oxidation of the organic compounds. Otherwise additional reactions may take place during pumping and in the heat exchanger. Moreover, the process water not completely used up could release undesirable reactions in the mixture.

When adding hydrogen peroxide, a powerful exothermic reaction will always be triggered and it will require cooling. Optimising the amount of hydrogen peroxide required in the process without bringing the reaction to a halt would result in substantial cost savings measures.



## Products and preliminary mass balance

The treatment plant should be geared towards treating the waste material to produce the maximum metal recovery that can immediately be sold to lower the cost of the treatment. In the case of the Theisenschlamm with its diverse chemical composition and compounds, some metals will not be able to be recovered economically.

Therefore, some of the residue will have to be managed. However, thanks to the good separation which can be achieved by treatment with hydrogen peroxide, the amount needing to be dumped will be less than 5%, corresponding to less than 11,000 t will need to be managed.

Based on total amount of 220,000 t of Theisenschlamm, the following yield will arise:

Gas phase: 106,600 t (of which 92,000 t CO<sub>2</sub>, 14,600 t steam)

Liquid phase: 505,100 t (of which 398,300 t water, 106,800 t salts)

Solid-phase: 110,100 t

Processing will require 501,800 t 60% H<sub>2</sub>O<sub>2</sub> solution. Hopefully the energy associated with the gas and liquid phase can be sold. Obviously, the liquid phase should be processed locally with an electrolytic process to get the valuable metals (Zn, Re, Cu) and sulphuric acid. Only relatively clean but salty water will remain, which if necessary can then undergo further treatment. Valuable metals and ballast materials would then have to be separated from the solid-phase, so that the lead concentrate can be used in a lead smelting plant.

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