9. Oxidation Treatment of Theisenschlamm

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Abstract

A low temperature oxidation process has been developed to separate lead from zinc in a complexly contaminated scrubber dust. The two-stage process consists of a grinding stage followed by contacting this material with a hydrogen peroxide solution. The resultant oxidation reaction is violently exothermic - the temperature rises spontaneously to approximately 96°C. The amount of solid phases remaining after completion of the reaction was reduced by approximately 40% and consisted largely of insoluble lead sulphate which retained the bulk of the radiation. Almost all of the zinc was placed into solution by this process as was the Cd, Re and Cu. The total PAH content of the original Theisenschlamm (468 μ g/g) was reduced to 11.25 μ g/g in the residual sediment and the PCDD/PCDF concentrations were reduced by approximately 40%. The radioactivity is almost completely concentrated in the solid phase. The method shows considerable promise for treatment of very fine-grained sulphide-bearing residues.

Introduction

Several attempts have been made to develop an hydrometallurgical or pyrometallurgical process to treat by extracting the valuable metal content of the Theisenschlamm residue, however none were found to be appropriate (LORENZ et al., 1992; LORENZ, 1994; WEILANDT, 1994). The treatment of this heterogeneous material requires a flexible technique that can deal with the complex characteristics of the material and at the same time minimize the cost of treatment and minimize the environmental impact. Conventional separation techniques cannot be readily applicable to this material due to its agglomerated state and its small grain size.

A series of experiments were carried out with a view to develop a low-temperature oxidation process in which the sulphide phases would be converted to sulphates,

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making it possible to separate the soluble zinc sulphate from the more stable lead sulphate. This possibility only exists if an oxidizing agent can act efficiently on the variety of complex phases present in the Theisenschlamm. The advantage of such an approach is that the zinc in solution could be recovered by standard metallurgical methods whereas the lead sulphate, including the radioactivity, could be processed by lead smelting (LEIPNER et al., 1994; WEILANDT, 1994).

In addition, several other characteristics of the oxidation process had to be monitored:

- 1. The partitioning of As, Cd, Tl (hazardous elements) and Ag, Ge,Re (valuable elements) between the soluble and solid fraction.
- 2. Any changes in the nature and concentrations of the organic compounds during the process.
- 3. The partitioning of the radionuclides between the reaction products.

The sample preparation techniques, the results of various oxidation experiments, the partitioning data and the evaluation of the reaction involving the organic compounds of the Theisenschlamm are presented in this chapter.

Oxidation Experiments

Samples of the Theisenschlamm were ground in an attritor and dried prior to treatment with hydrogen peroxide. The grinding was done to create fresh surfaces on the constituent particles which would be more reactive. Also, the reduction of the grain size would help to make the reaction more complete and more exothermic. Figure 1 is a flow sheet of the grinding and oxidation processes that were adopted as our standardized procedure.

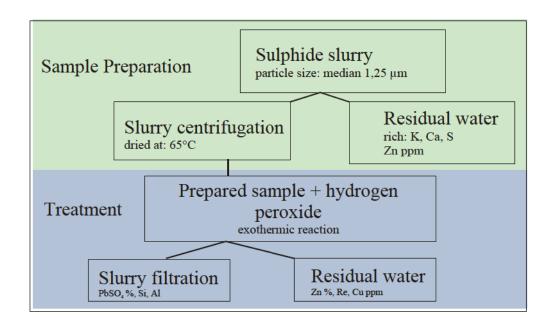


Figure 1 Schematic illustration of the grinding and oxidation procedure developed for TSOP

The flow process consists of two separate steps - a mechanical pre-treatment phase (grinding) and the oxidizing reaction *per se*. The whole process is referred to as the Theisenschlamm-Oxidation-Process (TSOP). The flow diagram also gives the conditions under which each step of the process was conducted.

Grinding Procedure and associated Chemical Changes

For the grinding procedure, 37 grams of the Theisenschlamm were placed in an attritor along with 300 ml of distilled water. The grinding medium consisted of roughly 2 kg of steel balls with a diameter of 2 mm. Mechanical erosion of the steel balls caused an iron contamination of the ground Theisenschlamm. The grinding time was standardized at one hour, after which the sample was dried. This procedure was used to produce the standard starting material for subsequent experiments. A substantial weight lost in excess of 14% was measured during the grinding step. Table 1 presents the chemical evaluation of the grinding process.

 Table 1:
 Chemical evaluation of the grinding process

Parameter	Ground Theisenschlamm [mg/kg]	Concentration in the grinding liquid [mg/l]	Proportion in solution [%]
Al	23,600	0.7	0.03
В	111	2	17.21
Ca	8,800	540	41.45
Cd	360	0.04	0.13
Co	80	0.51	6.85
Cr	890	0.51	0.66
Cu	14,100	0.12	0.01
Fe	30,850	0.84	0.03
K	6,700	290	33.31
Mg	2,500	98	31.14
Mn	670	12	17.13
Ni	510	2.2	4.74
Pb	122,000	3.6	0.03
TI	320	0.7	2.46
Zn	163,000	830	5.55
Stotal	113,000	1,500	13.28
Oil & grease	8,700		0

Shown is the concentration for a limited number of elements for the Theisenschlamm after grinding as well as the composition of the recovered liquid which can contain

elements in solution as well as matter in suspension. The proportion of each element that was found in the water phase is also presented in Table 1. This proportion varies from roughly 40% for Ca to almost 0 for Pb and Cu. It is clear that the composition of the Theisenschlamm before and after grinding differ considerably, however only the concentrations of the most easily water-soluble elements are affected - the concentrations of the elements of economic interest (e.g. Pb, Zn) or of environmental interest (e.g. Cd, Tl) are not significantly modified.

The Peroxide Reaction

A mass of 5 grams of the ground Theisenschlamm was then treated with 350 ml of 30% hydrogen peroxide solution. The slurry was continuously stirred magnetically and the temperature was monitored during the process. The resultant reaction was violent and strongly exothermic. At the peak of the reaction a temperature of 96°C was measured and the slurry began to fume and froth which required vigorous stirring to prevent the slurry from boiling over. After leaving the solution overnight, the slurry was filtered and the solid residue examined by diffraction and with scanning electron microscope (SEM). The chemical composition of the liquid was determined by ICP (experimental details MORENCY et al., 1998). The radioactive elements, as detected by alpha counting, and the Pb are preferentially concentrated in the sediment at the bottom of the beaker (solid product), whereas the zinc is found in solution.

Aging of the ground Theisenschlamm.

As mentioned, the reaction between the ground Theisenschlamm powder and the hydrogen peroxide is strongly exothermic. To check for the possible influence of aging on the ground material that could be related to an oxidation process, three groups of samples (10 samples total) were prepared as described above, and the dried powders were stored in an oven at 65°C for periods of one, two and three weeks respectively prior to reaction with the peroxide. The temperature-time relationships during reaction of these ten powders are illustrated on Figure 2.

The behaviour of all three groups of samples was the same except that the time for the reaction to occur is different for the three groups. The results seems to relate to an oxidation process with the static air environment for the ground Theisenschlamm when the sample is stored at 66°C for several weeks.

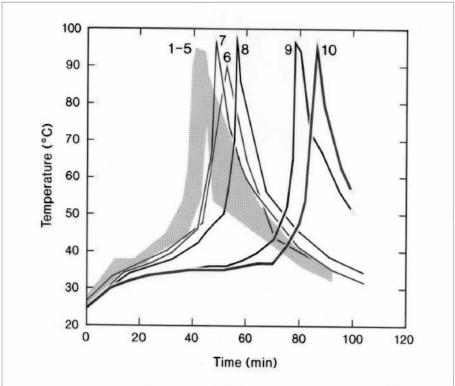


Figure 2: Time-temperature relationship during TSOP reaction for samples of different drying ages (65°C)

Results

Mineralogical changes resulting from the peroxide reaction

Figure 3 is a composite diffractogram showing the profile for the starting material prior to reaction, the residual solid after reaction, as well as a diffraction profile for the solid obtained by total evaporation of the liquid phase. The Theisenschlamm is shown to be a mixture of phases, predominantly galena, sphalerite/wurtzite (sulphides) and anglesite (sulphate), whereas the diffractogram of the solid product of the TSOP reaction indicates the presence of anglesite only. In particular, two peaks for the sulphides ZnS, (at $2\theta = 33.2^{\circ}$ and 35.7°), are visible on the ground Theisenschlamm curve whereas they are absent from the middle curve. The diffraction pattern for the liquid product is dominated by boyleite (zinc sulphate) since the liquid phase was almost completely clear after the reaction.

These results indicate that the zinc and lead sulphides are oxidized and the zinc is found in solution. It was determined that the lead sulphide is converted to lead sulphate which is a stable phase under surface conditions. It is probable that the negligible residual zinc in the solid is associated with a more stable phase and is not readily available for reaction with the hydrogen peroxide It has been shown that some grains in the Theisenschlamm residue are complete solid solution mixtures of Pb and Zn. It is therefore possible that an anglesite coating forms around the larger grains during reaction, thereby shielding the Zn from further dissolution.

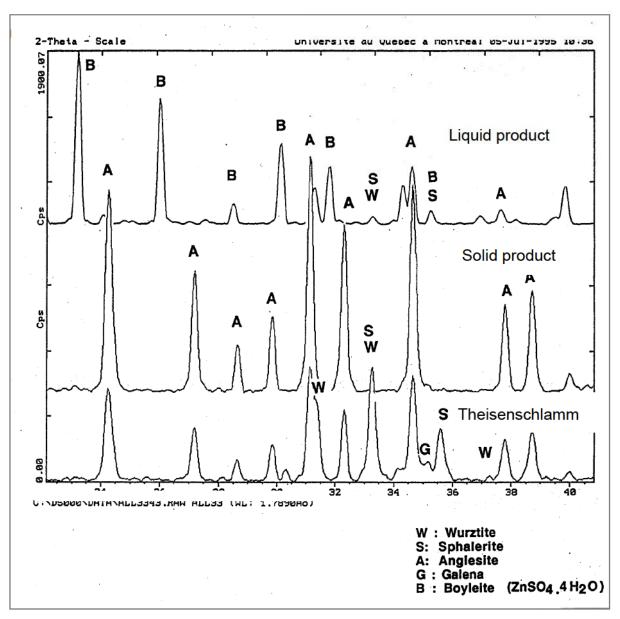


Figure 3: Composite diffractogram showing the profile for the starting material prior to reaction (Theisenschlamm), the solid product of the reaction, as well as a diffraction profile for the sediment obtained by total evaporation of the peroxide solution.

Effect of Peroxide Treatment on Particle Size

Figure 4 is a relative frequency distribution diagram for a sample of Theisenschlamm and the solid product of the reaction. The ground sample had a median diameter of $3.98~\mu m$ for the volume calculated results compared with a median value for the solid after TSOP treatment of $3.20~\mu m$.

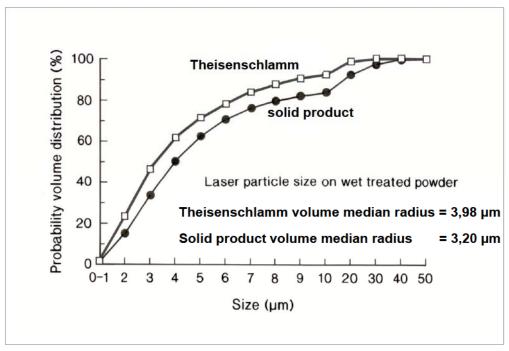


Figure 4: Relative grain size distribution for ground Theisenschlamm and the remaining solid product of TSOP treatment

Impact of the Peroxide Treatment on the Inorganic Chemistry

Table 2 presents results of analyses of solid products after treatment as well as the composition of ground Theisenschlamm and the composition of the residual liquid.

The most important feature of the results is seen by comparing the Pb:Zn ratio for the ground Theisenschlamm prior to treatment with that of the solid remaining after treatment, in the former the ratio is 0.75:1 whereas in the latter it is approximately 12:1 while the same ratio for the liquid phase is 1:700.

The percentage of the original mass in solution for each element was calculated by assuming 3 grams of solid remaining for 280 ml of liquid after the reaction. These values are shown graphically in Figure 6 in relationship to their concentrations in the Theisenschlamm. Results show that 93.7% of the zinc originally present was found in solution whereas the comparable figure for Pb is about 0.2%. In other words, the separation of Pb from Zn is almost complete. Pb, S, Si and Fe are the most important elements in the residual sediment, whereas in the liquid phase, the total of Zn + S is 92% of the total amount present, with Re and Cu being important associated elements.

Table 2: Composition of a typical sample of ground Theisenschlamm and the composition of the remains of the hydrogen peroxide solution after cessation of the reaction

	Ground Theisenshlamm Products after TSOP Reaction		OP Reaction
Element	[ha\a]	Solid [µg/g]	Liquid [mg/l]
Ag	520	810	n.d.
As	4,080	7,600	0.19
Cd	360	30	5.10
Cr	890	1,160	1.56
Cu	14,100	1,215	183.50
Fe	30,850	43,700	1.45
Hg	110	130	n.d.
Mn	670	580	5.82
Ni	510	360	4.57
Pb	122,000	182,000	3.75
Re	63	9	1.00
Sb	1,470	2,400	0.06
Se	720	320	8.40
Sn	17,200	26,500	n.d.
Th	2	3	n.d.
Ti	5,000	5,580	n.d.
TI	320	290	2.18
U	30	32	0.12
Zn	163,000	15,800	2,500
Stotal	113,000	39,900	1,680

n.d.: not detectable

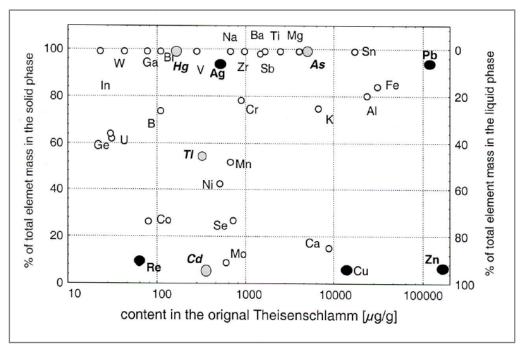


Figure 5: Element distribution pattern between the solid and the liquid phases after the TSOP treatment

Impact of the Peroxide Treatment on the Organic Chemistry

Results of the determination of the PAH concentrations (MORENCY et al., 1998) are presented in Table 3. The data show that the concentrations in the original material are much higher than in the solid residue of the oxydation process. Total PAH concentration (see Table 3) in the untreated material is 468.9 mg/kg, whereas in the residual sediment it is 11.25 mg/kg giving a reduction of almost 98%.

Table 3: Results of PAH measurements on ground Theisenschlamm and TSOP reaction products

Compound	Ground Theisenschlamm	Solid reaction product	Liquid product
	[µg/g]	[µg/g]	[µg/ml]
Naphtalene	1.9	0.20	0.0140
Acenaphtalene	0.3	0.03	0.0012
Fluorene	2.9	0.12	0.0033
Phenanthrene	111.7	0.04	0.0100
Anthracene	10.7	n.d.	0.0009
Fluoranthene	71.0	1.90	0.0070
Pyrene	74.5	2.31	0.0014
Benzo(a)antracene	21.2	1.16	n.d.
Chrysene	62.3	2.20	n.d.
Benzo(b)fluoranthene	45.6	1.64	n.d.
Benzo(k)fluoranthene	4.7	0.27	n.d.
Benzo(a)pyrene	18.0	0.57	n.d.
Dibenzo(a,h)antracene	1.2	n.d.	n.d.
Benzo(g,h,i)perylene	31.7	0.63	n.d.
Indo(1,2,3)pyrene	11.2	0.18	n.d.

n.d.: not detectable

The results of the identification of several categories of compounds by GC/MS analysis (MORENCY et al., 1998) were classified into groups and are presented in Table 4. The solid product has a chromatogramm which is dominated by the paraffines.

The high boiling temperature of the mixture has been reduced. The values in Table 4 clearly show the decrease in the concentration of aromatic compounds. Specifically, the quinoline/isoquinoline derivatives are absent and their alteration products, the aromatic amino compounds are present.

Table 4:	Results of GC/MS analyses of ground Theisenschlamm and TSOP reaction products
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Compound	Ground Theisen- schlamm	Solid product	Liquid product
Compound	[area/g sample]	[area/g sample]	[area/148 ml water]
Alkanes	4,927,739	1,689,739	51,504
Polycyclic aromates	21,691,242	617,529	17,612
Benzenederivates	415,116	495,526	411,736
Naphthalinederivates	1,860,532	399,127	1,776
Biphenyles and/or	00.074.005	4.040	4
dibenzofuranes	20,674,225	4,618	traces
Diphenylethanes	traces	9,607	57,720
Quinoline- and/or			
Isoquinolinederivatives	24,969	n.d.	n.d.
Aromatic amines	n.d.	12,787	n.d.
Dibenzothiophene-			
derivatives	5,672,415	69,959	n.d.
Fluorenone-9	431,204	4,729	traces
Benzenemethanol	43,781	40,865	38,776
Stryene	34,166	35,134	14,060

n.d.: not detectable to a limit of approx. 5-10 ng/component (full scan mode)

The analysis of the extract from the liquid residue indicates a low concentration of hydrocarbons. Water soluble substances, such as benzenemethanol and benzene-dicarbonyl acids are predominant with volatile compounds such as the xylenes also present. The concentration of the toxicologically relevant N- and S-heterocyclic compounds has been significantly reduced in the solid while the liquid product contains insignificant quantities of hydrocarbons, predominantly alkanes, some low boiling aromatics and water soluble compounds such as phthalates.

The results of the PCDD/PCDF analyses of the original material and the solid product are listed in Table 5. The sum total concentration of each group is shown in ng/g of dried material. A decrease in PCDD/PCDF concentration after peroxide treatment is observed, particularily in the smaller chlorosubstituted isomer range. It is possible that some of the more volatile (tetrachloro-substituted) isomers might have been overlooked during the analysis - this is because an open beaker was used during the exothermic oxidation reaction.

Table 5: Results of PCDD/PCDF analyses on ground Theisenschlamm and the sediment remaining after TSOP treatment. Also shown are the International Toxicity Equivalents (ITE) expressed in ng/g.

	Ground Theisenschlamm [ng/g];	Solid product [ng/g]	
Sum TCDF	86,0	47,1	
Sum PeCDF	40,3	30,1	
Sum HxCDF	10,5	14,7	
Sum HpCDF	8,4	6,2	
OCDF	1,4	2,5	
Sum PCDF	146,6	100,6	
Sum TCDD	5,9	0,7	
Sum PeCDD	0,8	1,1	
Sum HxCDD	1,8	0,3	
Sum HpCDD	1,9	n.d.	
OCDD	5,5	n.d.	
Sum PCDD	15,8	2,1	
Sum PCDD/PCDF	162,4	102,7	
Toxicity Equivalents [ng iTE/kg]			
Sum PCDD/PCDF	171,0	140,1	

n.d: not detectable lower than approximatly 50 pg.

A chemical change, involving the degradation or transformation of the dioxins and furans would produce changes in the isomeric pattern. However, when compared with Theisenschlamm sample, the relative proportion of the PCDD/PCDF compounds in the product was the same - only the total amount varies.

Radioactivity

Alpha and gamma spectroscopy (MORENCY et al., 1998) was carried out on the ground Theisenschlamm as well as on both TSOP reaction products to determine the activity of ²¹⁰Po and ²¹⁰Pb respectively. The radioactivity value associated with ²¹⁰Po in the Theisenschlamm sample prior to reaction was determined to be 16.6 kBq/kg. After the peroxide treatment, the value in the residual solid increased to 19.9 kBq/kg whereas the value for the liquid phase was 0.2 kBq/l. The radioactivity value associated with ²¹⁰Pb in the starting material prior to reaction was determined to be 22.1 kBq/kg, whereas in the solid and the liquid phase the values were 27.1 kBq/kg and 0.004 kBq/l respectively.

Both techniques yielded comparable results, indicating that the radioactivity is concentrated with the solid and in particular in the lead sulphate phase, after the

peroxide treatment. The concentration level in the liquid phase is very low and thus the treatment can be considered to have been successful.

Discussion

Peroxide oxidation has occasionally been used as a technique for conditioning the surface of sulphide-bearing mine waste prior to application of coatings or other treatments (MAKI et al., 1995; GEORGOPOULOU et al., 1995). The mine waste samples were also ground prior to treatment but no details were given on the characteristics related to the size distribution, mean or median. On the other hand the median particle diameter of Theisenschlamm aggregates is approximately 1 µm and the particles which constitute the aggregates are smaller still. Thus it is likely that the mine waste, even after grinding, is still coarser than the Theisenschlamm. An additional difference in the process is related to the concentration of the hydrogen peroxide used (9%) and the solid:liquid ratio in which 30 mg of powder in 200 ml of peroxide Maki et al. (1995). In our process 5 g of powder in 350 ml of peroxide at 30% concentration was used. These significant differences, when combined with the finer particle size of the Theisenchlamm and the poorly crystalline nature of the sulphides of the scrubber dust, resulted in an exothermic reaction as described above which was not noted in the other two studies.

A peroxide treatment as described here has considerable remediation potential, particularily for very fine-grained material. Lead, zinc and sulphur are the most important components of the Theisenschlamm. The separation of the Zn from the Pb not only reduces the mass of the waste it also generates an economically useful product which can be used as input feedstock to other industrial processes. Hydrometallurgical and pyrometallurgical methods require significant capital investment which would not be economically feasible considering the relatively small amount of material to be treated (LEIPNER et al., 1991; LORENZ et al., 1992).

Conclusions

- Hydrogen peroxide is an excellent oxiding agent for the Theisenschlamm. It
 caused the near complete separation of the Zn from the Pb. This yields an
 hydrated zinc sulphate that can be used in an electrolytic process for zinc recovery
 and products with an added value. In addition, lead sulphate can be used in lead
 smelting for products with added values.
- The small amount of Zn remaining in the solid residue after treatment does not appear to be accessible at the grain size at which the experiments were conducted.
- The radioactivity is associated with the solid phase (i.e. lead sulphate).

- The peroxide treatment reduces the concentration of PAH in the solid residue by almost 98% and the PCDD/PCDF concentrations by approximately 40%.
- After peroxide treatment, the liquid phase contains insignificantly small quantities
 of hydrocarbons, predominantly alkanes, some low boiling aromatics and water
 soluble compounds such as phthalates.

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UFZ-Bericht Nr. 22/2001

Fine-grained residues from copper smelting and their environmental impacts

A case study from the Mansfeld District, Germany

edited by:

BIRGIT DAUS and HOLGER WEISS