4. Mineralogical and Physical Characterization of Theisenschlamm

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Abstract

A physical and mineralogical description of Theisenschlamm is presented. This material was generated as a by-product during extraction of copper from the Kupferschiefer formation a mineralized Permian black shale in Sachsen-Anhalt, Germany. The Theisenschlamm consists of sulphide grains which are a complex solid solution of Pb, Zn, Cu and Fe. The crystal structures are modified forms of galena and sphalerite/ wurtzite. Variations in the X-ray diffraction peak positions of these minerals reflect the intensive ionic substitution that underwent the lattice structures of these phases. Anglesite is a secondary phase associated with the alteration through oxidation of the lead sulphides in the slurry. The original particles have a median diameter of 1.25 µm, however these particles are themselves aggregates of still smaller particles, typically of sub-micron in size. In this chapter we describe the physical properties of the Theisenschlamm, including the mineralogy, radioactivity and grain size as well as the micro-chemical composition and variation.

X-Ray Diffraction

All inorganic compounds discussed in this chapter are referred to as "minerals", however it is recognized that those which formed rapidly during the smelting process are more properly termed "chemical compounds" since they did not form in a "natural" manner. In particular, zinc sulphides (ZnS) is used here to refer to both naturally occurring sphalerite or wurtzite, as distinguished by X-ray diffraction as well as zinc rich sulphides with a sphalerite-type structure that were produced in the smelter. Similarly galena refers to the naturally occurring mineral lead sulphide (PbS) as well as to the artifically produced Pb rich sulphides, containing other elements such as Zn, Cu and others, in its structure. Anglesite ($PbSO_4$) is similarly employed to describe any lead sulphates.

X-ray diffraction (WEISS et al., 1997) is used to obtain the main mineral phases of the Theisenschlamm. Figure 1 is a diffractogram scan for a Theisenschlamm sample for

which the background noise was substracted, otherwise a "camel hump" is present between 2θ = 25° and 2θ = 45° indicating the amorphous fraction for the sample. In other figures, a smoothing of the curve is made for a better presentation of the data. The peak index lines are indicative of the presence of those associated chemical or mineralogical phases given in the captions of the diagram. The predominant phases identified on the diffractogram are a sulphate ($PbSO_4$) as well as the sulphides PbS and ZnS.

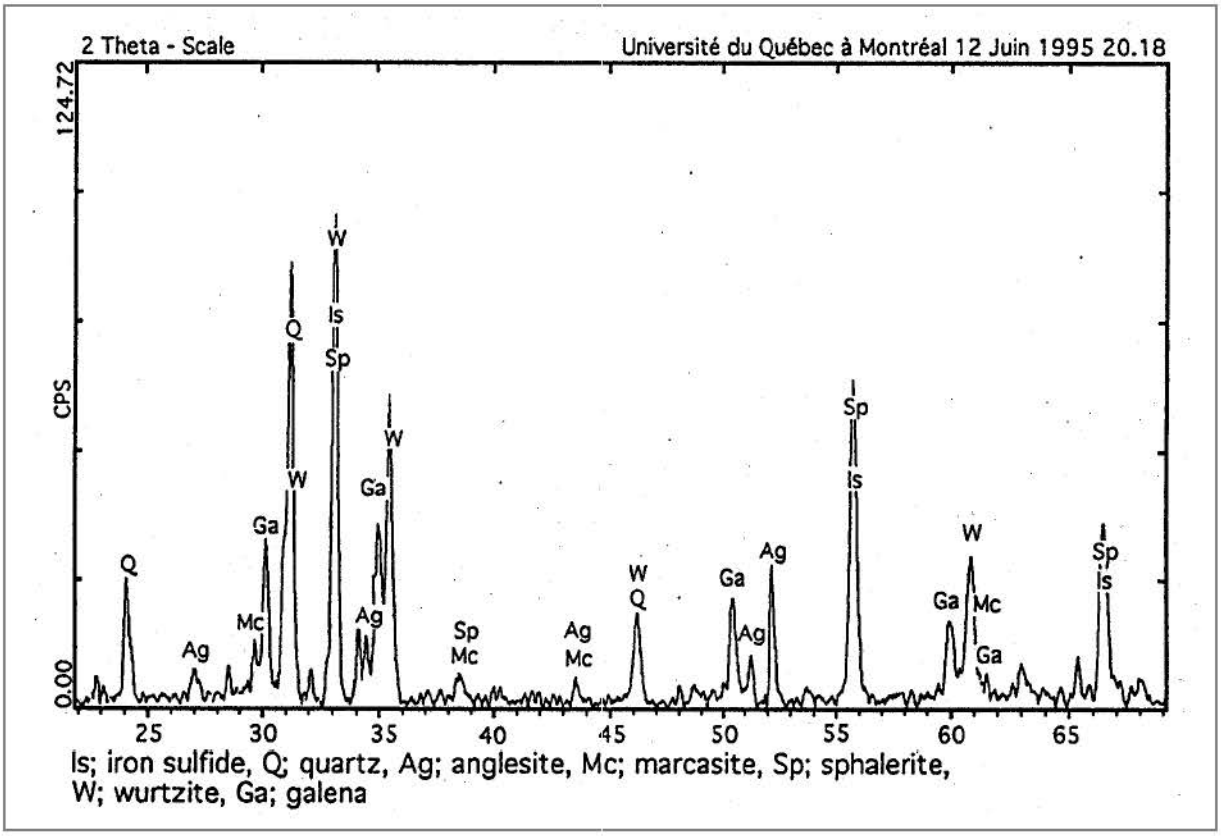


Figure 1: *2θ diffractogram scan for Theisenschlamm (Weiss, 1997). The peaks have been indexed using the following code: Is = iron sulphide; Q = quartz; Ag = anglesite; Mc = marcasite; Sp = sphalerite; W = wurtzite; Ga = galena*

Figure 2 is a comparaison between two diffractograms of representative samples of Theisenschlamm. Two features are immediately apparent:

1. The diffractograms are not identical despite the fact that they are splits of the same material. Not only are the positions of the peaks different from one another, but the relative heights also differ. The differences are significant and even the disappearance of some peaks was noted in some diffraction patterns. A similar effect was noted when the powder used to produce the XRD pattern was removed by washing and then remounted.
2. The position of the peaks has been offset with respect to the standard ASTM values for these natural minerals.

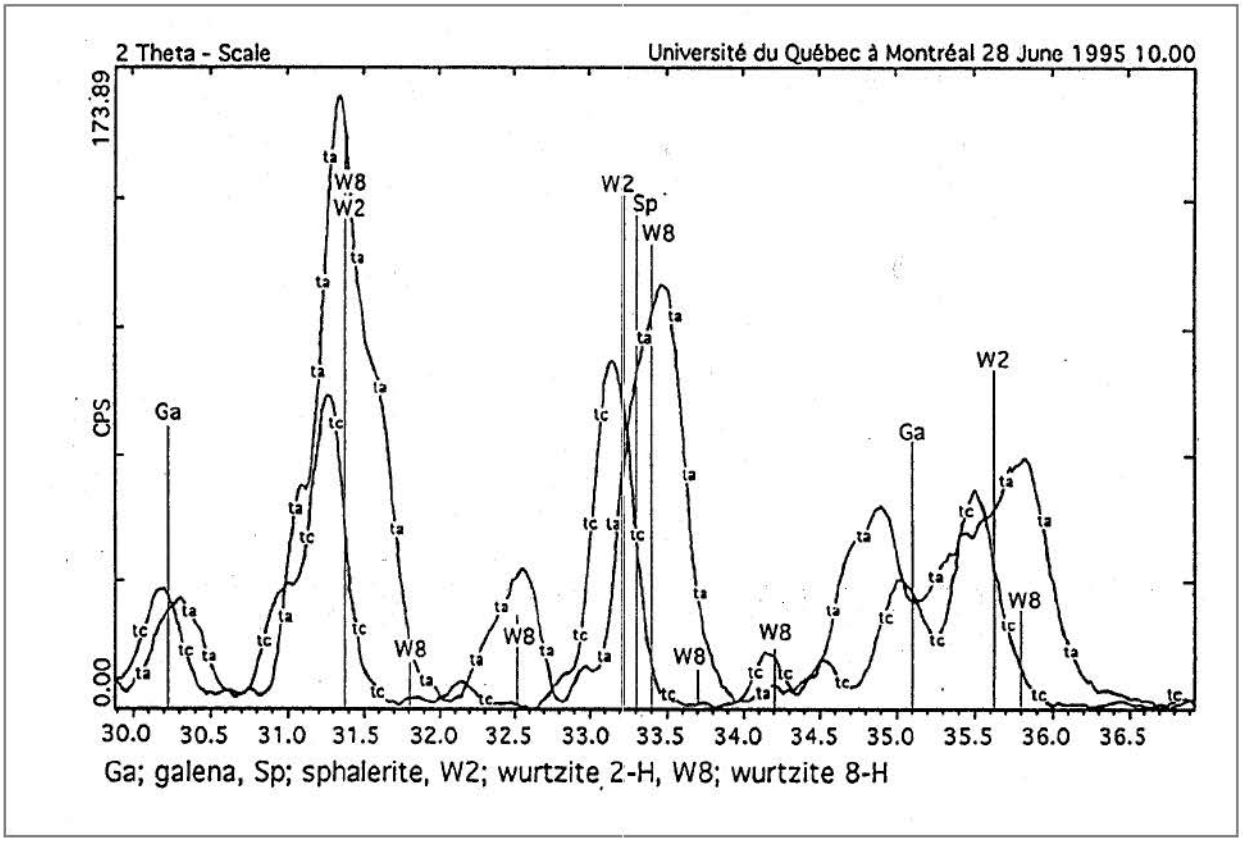


Figure 2: *Enlargement of a portion of a diffractogram for two samples of Theisenschlamm. Legend: Ga = galena; Sp = sphalerite; W2 = wurtzite 2-H; W8 = wurtzite 8-H*

Variation in peak heights can be caused by preferential orientation of particles during the mounting process (DAVIS, 1987; MANIAR & COOKE, 1987), but mounting cannot explain the shift in position of the various peaks. This feature indicates that the Theisenschlamm is an heterogeneous material and must be variable even on the scale of the individual sub-micron sized particle.

In spite of the complexity shown by the individual minor phases, examination of numerous X-ray diffraction patterns of different samples indicated that the mineral abundance calculated for the Theisenschlamm vary within narrow limits. Table 5 gives the approximate concentrations of the major phases in the powder and clearly shows an abundance of sulphides and sulphates. The percentages were determined by calculation of the area under the curve for selected peaks for each mineral and because the peak height variations these values are only semi-quantitative.

Table 5: *Approximate concentration of mineral phases in the Theisenschlamm [vol-%]*

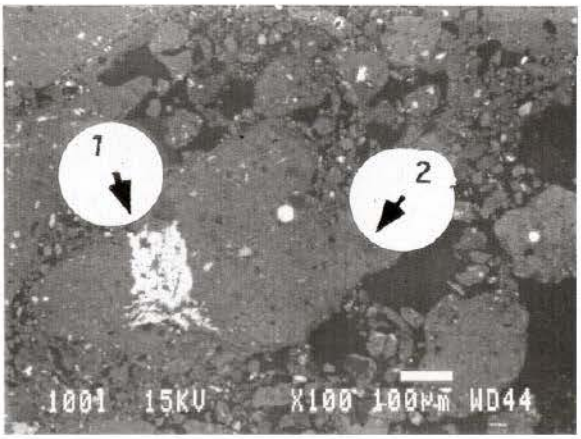
Mineral	Volume %
Wurtzite	19.5
Sphalerite	17.5
Galena	6.9
Anglesite	6.3
Quartz	2.5
Amorphous	38
Others	8

Scanning electron microscopy (SEM) results

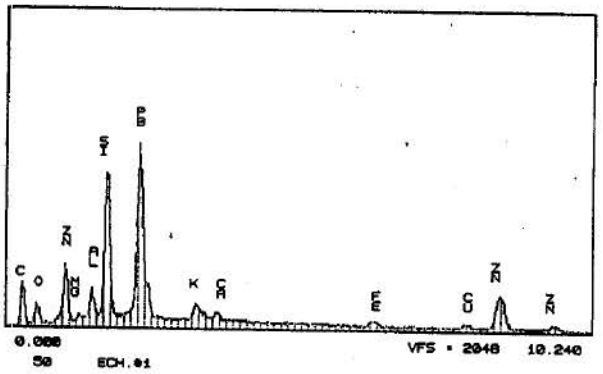
The Scanning Electron Microscopy (SEM) was used to determine the micro-chemical composition and element distribution as well as the texture and size of the different chemical phases. Samples of a dried slurry powder were embedded in a polymer from which a polished section was obtained and coated with either gold or carbon. This sample preparation technique gives a cross section of the component particles and enhances the textural and morphological characteristics of the grain.

Two populations of fragments can be observed on Figure 3a which is an image at low magnification (100x) (WEISS et al., 1997). A bright (white) fraction of variable size consisting of large agglomerates of 100 µm, less frequent spheres of 10 µm and a large population of needle-like grains, typically 5 µm in length by 1 µm wide, which appear on the image as little white spots. The other, darker population consists of gray large irregular shaped agglomerates several hundred microns in size. The texture of the fragments aggregates and/or agglomerates are porous and no uniformly solid grains are evident.

The analytical spectrum for the bright fraction is represented on Figure 3b and shows the presence of significant Pb with lesser amounts of Zn and Si and minor amounts of other elements. This is interpreted to be indicative of the presence of lead sulphide, which has also incorporated some Zn. The remaining elements of the spectrum could either originate from the filled interstices of the fragment or from the a signal coming from below the thin analyzing surface.



a)



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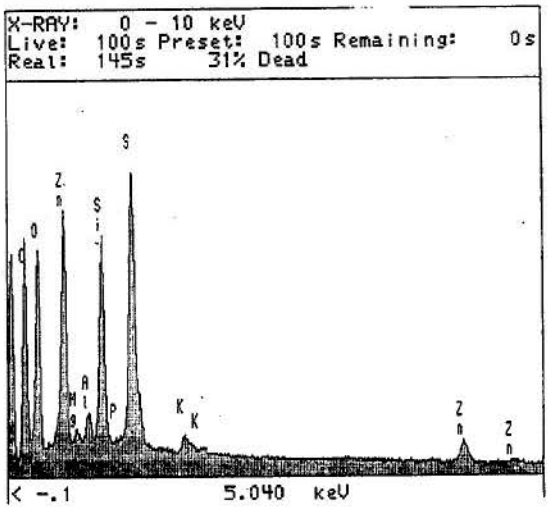

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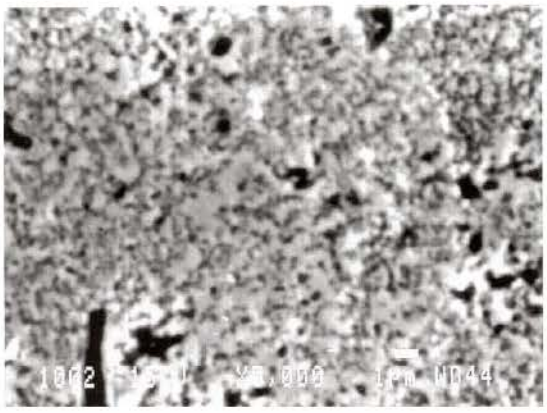
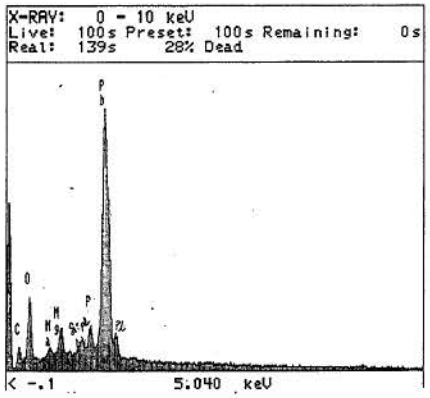


d)



e)

Figure 3: *a) SEM image at low magnification (100x) showing two populations of fragments*
b) analytical spectrum for the bright fragment seen in Fig 3a (arrow 1)
c) analytical spectrum for a grey agglomerate seen in Fig 3a (arrow 2)
d) image of a large bright fragment of 100 µm seen in Fig 3a (arrow 1), enlarged to 5000x
e) analysis of the fragment shown in Fig 3d

The gray agglomerates yield a spectrum given by Figure 3c which is characterized by a predominance of zinc with sulphur (ZnS sphalerite or wurtzite). Quartz (SiO_2) is often present in small solid grains, but amorphous silica appears to be scattered throughout the sample. Small concentrations of Al, Mg and K were also detected. In this particular instance, the apparent absence of lead is related to the low voltage used for the analysis and the gold plating used on the polished sections. Lead is very abundant in the powder as demonstrated by element mapping (see Figure 5).

An image of a large (100 µm) bright fragment, enlarged to 5,000x, is illustrated in Figure 3d with the matching analyses on Figure 3e. The fragment is porous and/or constituted by an agglomeration of irregular sub-micron size particles. The particle has elevated values for both lead and oxygen, indicating the presence of anglesite.

A needle-like fragment embedded in a gray agglomerate was enlarged to 20,000x and is illustrated on the photomicrograph of Figure 4. On closer examination it is seen that the needle is not a homogeneous solid but rather seems to be made of even finer particles which combine to form a needle-shaped agglomeration. The finer particles, which have diameters < 0.1 µm are disperse into the gray material adjacent to the needle. This texture, grain size and compositional variation could explain the reflection shifts in the diffraction pattern mentioned above and the diffuse nature of the mapping images (Figure 5).

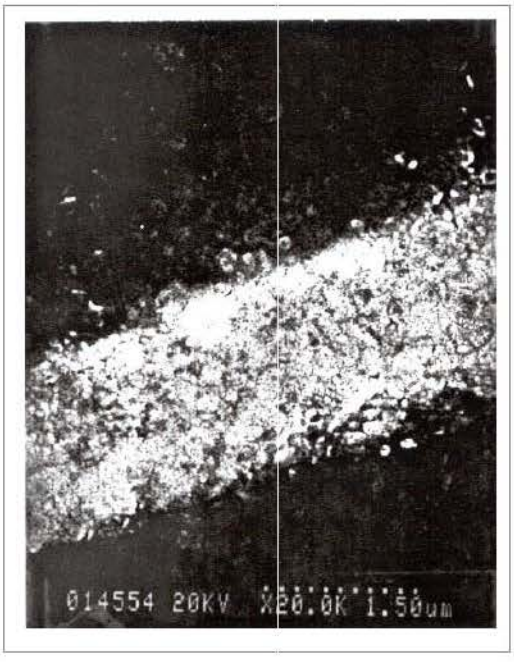


Figure 4: *SEM photomicrograph of a needle-like fragment embedded in a grey agglomerate, enlarged to 20,000x*

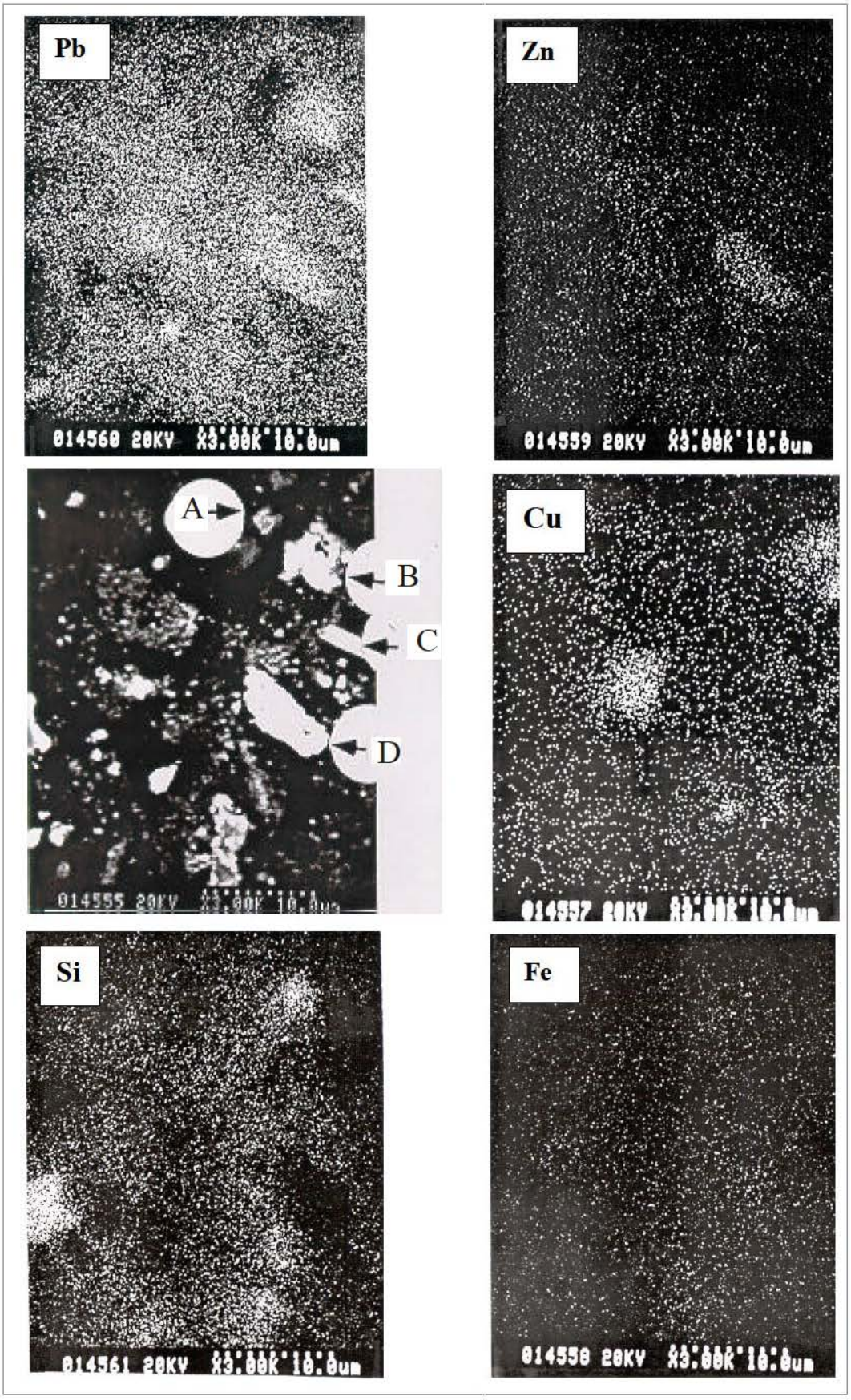


Figure 5: *Element mapping as indicated by back-scatter electron imagery*

The element mapping of Figure 5 associates the element with individual grains and illustrates the distribution and association for a selected area. Lead displays a strong signal throughout the analyzed area, often more concentrated on particular fragments (grains), but never defining a sharp outline. In all cases the grains boundaries are fuzzy. Zinc is not as abundant and its distribution is more uniform over the area considered. In general zinc is associated with the smallest fractions and is therefore more evenly distributed in other spots its absence or concentration can be associated with specific grains or fragments. Iron is also distributed throughout with very little variation.

The identified fragments on the photomicrograph (Figure 5, middle, left) have the following element associations:

B = Pb, Cu;

D = Pb, Zn, Fe;

A and C = Si, Pb.

It should be noted that the samples moved slightly during the mapping procedure, as a result the overlap is not exactly matching.

In conclusion the SEM evaluation indicates that the Theisenschlamm material contains fragments which are aggregates and/or agglomerates of extremely fine grained particles. In some cases these agglomerations are rich in lead and in other cases they are a mixture of Pb, Zn, Cu and Fe. The bright agglomerations generally have a lead sulphide or sulphate composition. The zinc sulphides do not form large fragments and as a result the zinc is more uniformly disseminated throughout the powder and forms the gray matrix in most sections. The multi-element composition of some of the sulphides indicates that they have undergone extensive substitution, a fact already alluded to in association with the X-ray peak shifts on the diffractograms.

Density and Grain Size

The density values of 2.92 g/cm^3 for the Theisenschlamm is low when compared with the known values of the individual identified phases. Sphalerite (ZnS), anglesite ($PbSO_4$) and galena (PbS) have densities of approximately 4.1, 6.4 and 7.6 g/cm^3 respectively and, according to X-Ray data these minerals constitute approximately 50% of the samples. The low density figures are almost certainly related to the porous nature of the fragments and agglomerates in the Theisenschlamm and also to the 40% of amorphous material present in the slurry. Figure 6 illustrates the grain size distribution for the Theisenschlamm - the median and mean diameters of the component particles are 1.25 µm and 1.55 µm respectively. It should be remembered that the laser instrument measures the diameter of the agglomerations of particles and not necessarily that of the particles themselves.

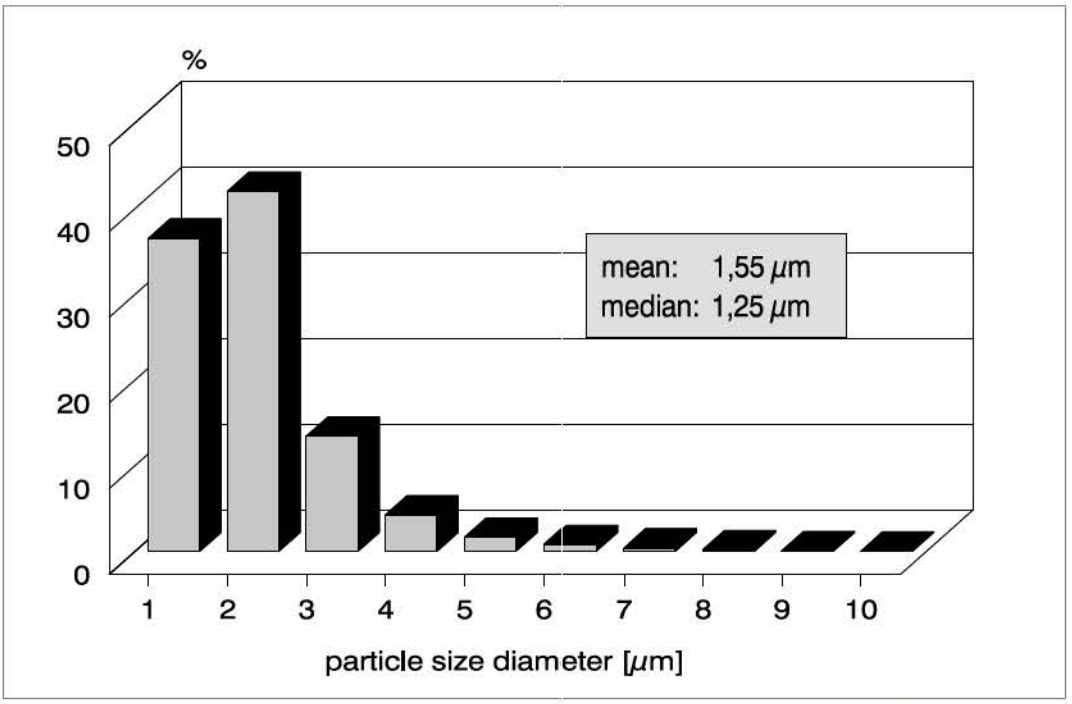


Figure 6: *Particle size distribution for a representative sample of the Theisenschlamm*

The risk of particle deposition of such small particles in the human respiration system should be mentioned Particles with diameters of 1 to 5 µm corresponding to the bulk size distribution of the Theisenschlamm can make its way and settle down in the peripheral bronchial tree (Table 6). Therefore the management of this residue should include these health factors.

Table 6: *Aerosole, relation between particle diameter, deposition place and mechanism of deposition*

particel diameter	place of deposition	mechanism of deposition
< 1 µm	expiration	gaseous phase
1 - 5 µm	periphereal bronchial tree	sedimentation
5 - 10 µm	upper respiration system and central bronchial tree	inert impact
> 10 µm	upper respiration system	

Radioactivity

The alpha spectrometry technique yielded concentrations of 32.9 µg/g ± 0.9 of ^{238}U and 2.1 µg/g ± 0.8 of ^{232}Th.

Alpha spectrometry measurements yielded a ^{210}Po activity of 16.6 kBq/kg; measurements by high resolution gamma spectrometry for ^{210}Pb yielded a value of 22.1 kBq/kg.

But as can be seen in the Figure 7 the risk based on the lead concentration is more critical with respect to the ADI-values (Annual Limit of Intake). The Theisenschlamm is not only a dangerous residue based on its heavy metal content and organic toxic compounds but also because of the associated radioactivity of the substance.

^{210}Pb / ^{210}Po in equlibrium:	1250 Bq
⇒	**22 g Theisenschlamm / a**
respiration volume:	1,3 m^3 / h
working time:	2000 h / a
⇒	**8,5 mg Theisenschlamm / m^3 air**
MAK-value for lead:	0,1 mg / m^3 air
⇒	**0,85 mg Theisenschlamm / m^3 air**

Figure 7: *Theisenschlamm - Inhalation (Annual Limit of Intake (ALI) for adults without professional radiation exposure)*

Discussion

The X-ray diffraction study indicates that sphalerite, wurtzite and galena are the dominant phases present in the Theisenschlamm. Amorphous material is also an important fraction of the material. The X-ray peaks of the mineral phases present in the Theisenschlamm, with the exception of anglesite, are difficult to index properly. This fact is believed to be caused by extensive ionic substitution. The SEM study identified two main populations of particles consisting of PbS or $PbSO_4$ and the other of ZnS, the Zn-bearing particles being smaller. The $PbSO_4$ is believed to be of secondary origin.

The Theisenschlamm consists of particles which have a much lower density than would be expected, considering the minerals identified and their abundance. This is attributed to the porous nature of the grains and agglomerates as well as the amorphous nature of the substances. The SEM results show that the grain size of the particles for the Theisenschlamm is variable. Particles ranging in size up to 100 µm were observed,

however the measured median diameter is 1.25 µm. The SEM data also reveal that the particles, whatever their size, are themselves agglomerates consisting of a collage of sub-micron-size particles.

The results of both alpha and gamma spectrometry confirmed the previously reported values for the radioactivity. This high radioactivity is due to the presence of ^{210}Pb in the slurry. This ^{210}Pb in turn decays to ^{210}Po; an equilibrium is reached after approximately 2 years. Due to the presence of these nuclides, the Theisenschlamm represents an additional radio-ecological risk (BUNDESAMT FÜR STRAHLENSCHUTZ, 1992; BUNDESAMT FÜR STRAHLENSCHUTZ 1994; LEHMANN, 1994; MINISTERIUM FÜR FÜR UMWELT UND NATURSCHUTZ DES LANDES SACHSEN-ANHALT, 1994).

References

BUNDESAMT FÜR STRAHLENSCHUTZ (1992): Radiologische Erfassung, Untersuchung und Bewertung bergbaulicher Altlasten.- BfS-Schriften 8/92, Salzgitter

BUNDESAMT FÜR STRAHLENSCHUTZ (1994): Radiologische Erfassung, Untersuchung und Bewertung bergbaulicher Altlasten.- BfS-IB 7, Salzgitter

BUNDESMINISTER FÜR UMWELT, NATURSCHUTZ UND REAKTORSICHERHEIT (ed) (1992): Bericht der Bund/Länder-Arbeitsgruppe DIOXINE. Rechtsnormen, Richtwerte, Handlungsempfehlungen, Meßprogramme, Meßwerte und Forschungsprogramme.- Bonn,

DAVIS, B. (1987): Quantitative determination of mineral content of geological samples by X-ray diffraction: discussion. American Mineralogist, 72, 438-441.

LEHMANN, H. (1994): Gefährdungspotential der Theisenschlämme.- In: Sanierungsverbund Mansfeld e.V. (Ed.): Theisenschlamm-Tagungsband zum Kolloquium vom 7.12.93; Mansfeld

MANIAR, P.D. & COOKE, G.A. (1987): Modal analysis of granitoids by quantitative X-ray diffraction. American Mineralogist, 72, 43-437.

Ministerium für Umwelt und Naturschutz des Landes Sachsen-Anhalt (1994): Umweltbericht 1993 des Landes Sachsen-Anhalt; Magdeburg

WEISS, H., MORENCY, M., FREYER, K., BOURNE, J., FONTAINE, D.,GALEB, B., MINEAU, R., MÖDER, M., MORGENSTERN, P., POPP, P., PREDA, M., TREUTLER, H.-CHR. & WENNRICH, R. (1997): Physical and Chemical Characterization of a complexly contaminated scrubber dust- a by-product of copper srnelting in Sachsen-Anhalt, Germany.- Sci. Tot. Environ. 203, 65 – 78

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Fine-grained residues from copper smelting and their environmental impacts

A case study from the Mansfeld District, Germany

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