

## RESEARCH IN PRESSURE LEACHING†

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### SYNOPSIS

This is a summary of investigations in the field of pressure leaching carried out at the Institute for Extractive Metallurgy of the Technical University of Berlin-West during the last seven years. The efficient dispersion of gas in a liquid and its dissolutions as well as the events at the phase boundary when leaching ZnS are reported. At the end two examples are given for the use of pressure leaching in the processing of smelter by-products.

### INTRODUCTION

About 20 years ago, experiments were independently started in Canada and in Berlin on the subject of dissolving sulfidic ores without preliminary treatment by means of leaching under increased oxygen pressure. In Canada ammoniacal solutions were mainly employed, and F. A. Forward and his co-workers were successful in applying this process on a large industrial scale<sup>1, 2</sup>. This process is used in Fort Saskatchewan to produce about 15,000 tons of Ni per year. In Berlin, investigations were started on leaching with acid solutions<sup>3, 4</sup>. This process had also been used on a large industrial scale in the U.S.A., but the choice of unfavourable working conditions led to great difficulties, and to giving up this process for industrial use.

Later on in Berlin work was carried out especially on the kinetics of pressure leaching<sup>5, 6, 7, 8, 9</sup> and its applications to the processing of smelter by-products, in particular of mattes and speisses<sup>10, 11, 12, 13, 14</sup>.

The dissolution of ores and by-products can be subdivided into four steps:

1. the efficient dispersion of the gas, so that its dissolution occurs over as great a surface area as possible, since only the dissolved oxygen reacts with the solid,
2. the suspension of the solid, so that the entire surface can take part in the reaction,
3. the phase boundary reaction,
4. the removal of the reaction products.

The first two steps belong to the field of process engineering and will be discussed from this point of view. The aim of these experiments<sup>15</sup> was to find out first of all the limits of efficiency of self-sucking stirrers in solutions of low viscosity with regard to the mass transfer. In addition, the effect of ultrasonics in the same reaction system was studied.

The experiments were carried out in a lucite container as shown in Fig. 1. Four baffles of 0.1 d width were in the stirring vessel. The height of these baffles was adjustable. For every experiment one litre of liquid was used. An infinitely variable direct current motor, which was fixed with a hollow shaft, served as the driving power for the stirrer.

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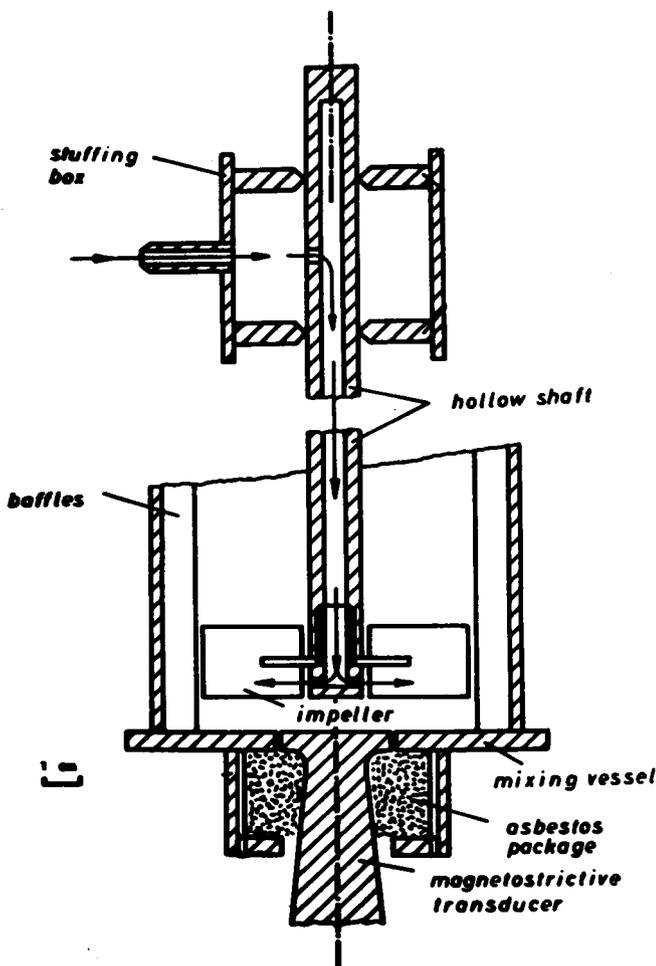


Fig. 1—Experimental equipment

In order to be able to determine the amount of gas taken in by the hollow stirrer, the suction hole of the hollow shaft was connected to a stuffing box with a gas-flow meter attached. In addition, it was possible to feed the hollow stirrer during the experiments with oxygen out of a pressure tank, so that the amount of gas could be regulated independently of the natural suction of the stirrer.

For experiments on the influence of ultrasonics, the stamp-like, sound-radiating part of the oscillator was built in to the bottom of the stirring vessel, so that the flow conditions were not altered and exact comparisons could be made.

As a model for the mass transfer from gas to liquid the reaction  $\text{SO}_3^{2-} + 1/2 \text{O}_2 \rightarrow \text{SO}_4^{2-}$  was used, which proceeds so rapidly, that the rate limiting

step is the dissolution of oxygen. The dissolution of solid iodine in very dilute aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ -solution served as a model for the mass transfer from solid to liquid.

The leaching of  $\text{Cu}_3\text{As}$  in ammoniacal solution with oxygen was chosen as the model for dissolution processes in which all three phases are involved. The low activation energy of about 4.4 kcal/Mol indicates that diffusion exerts the main influence<sup>12</sup>.

First of all the dissolution of molecular oxygen in the solution will be considered. The first requirement is a sufficient solubility of the gas in the liquid. The solubility is determined by the temperature, independently of the partial pressure, and shows a minimum (Fig. 2). Other compounds dissolved in water, such as acids, bases or salts, likewise decrease the solubility of the oxygen, as shown in Fig. 3.

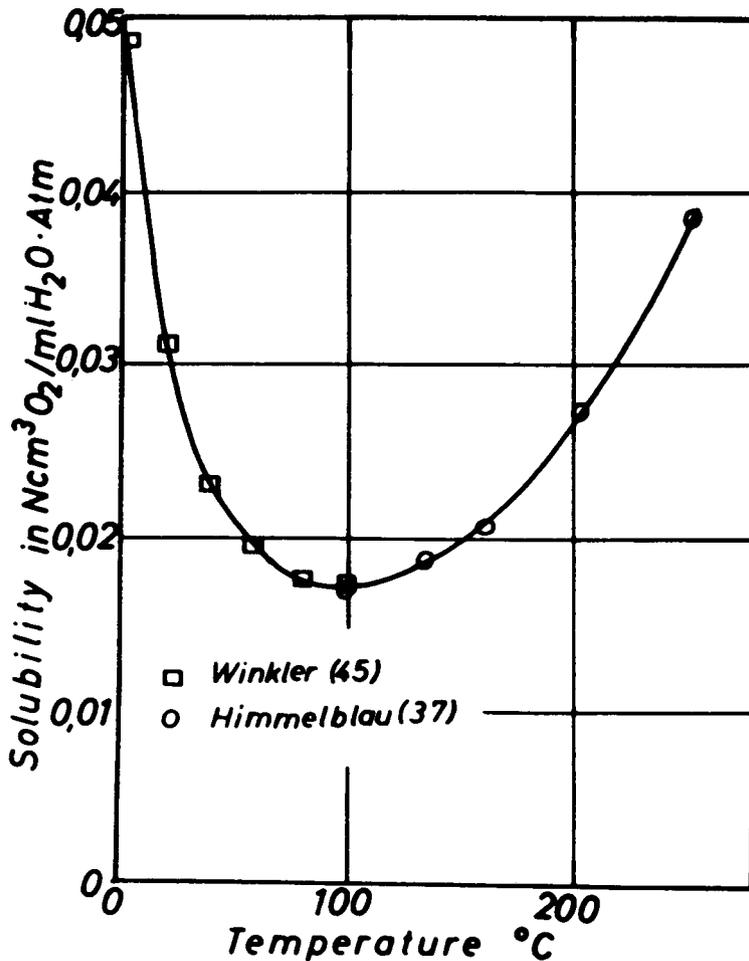
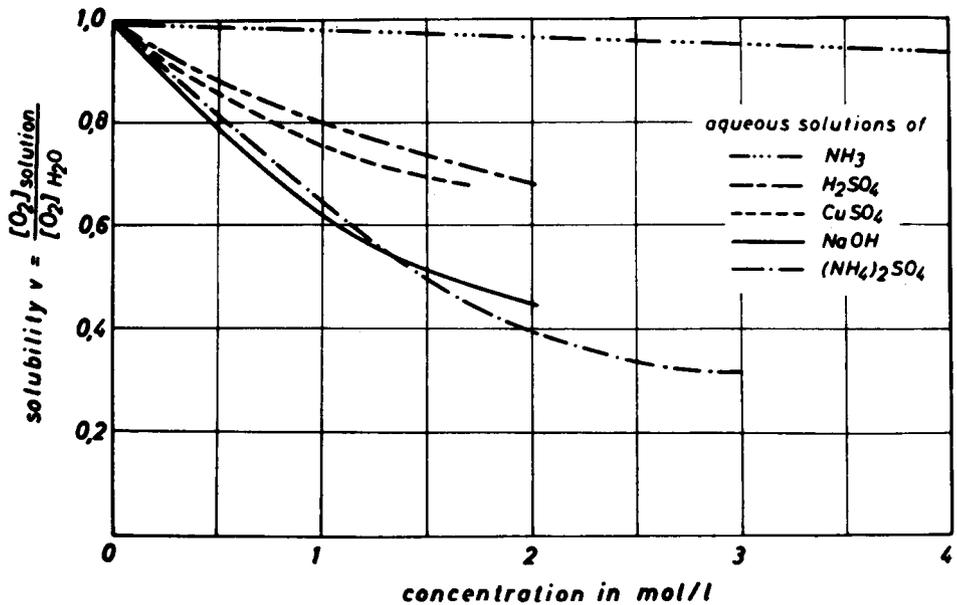


Fig. 2—Solubility of  $\text{O}_2$  in water as a function of temperature

Fig. 3—Solubility of O<sub>2</sub> in different aqueous solutions

Furthermore, the rate of this step can be limited by a deficiency of supplied oxygen. Altogether six different types of stirrers were tested, which are presented schematically in Fig. 4. They suck different amounts of gas as a function of the rotation speed as Fig. 5 shows. The letters in Fig. 5 correspond to the different stirrer types as drawn in Fig. 4.

Not only the amount of gas, but also the diameter of the bubbles is dependent on the rotation speed. Fig. 6 shows a gas-liquid mixture with a gas flow rate of 90 Normal litres per hour. The enlargement of a detail in Fig. 7 shows clearly the single bubbles. The analysis of numerous experiments led to the curve in Fig. 8, which indicates, that the bubbles reach a minimum size of about 0.05 mm in diameter. A further increase of rotation speed has no more effect.

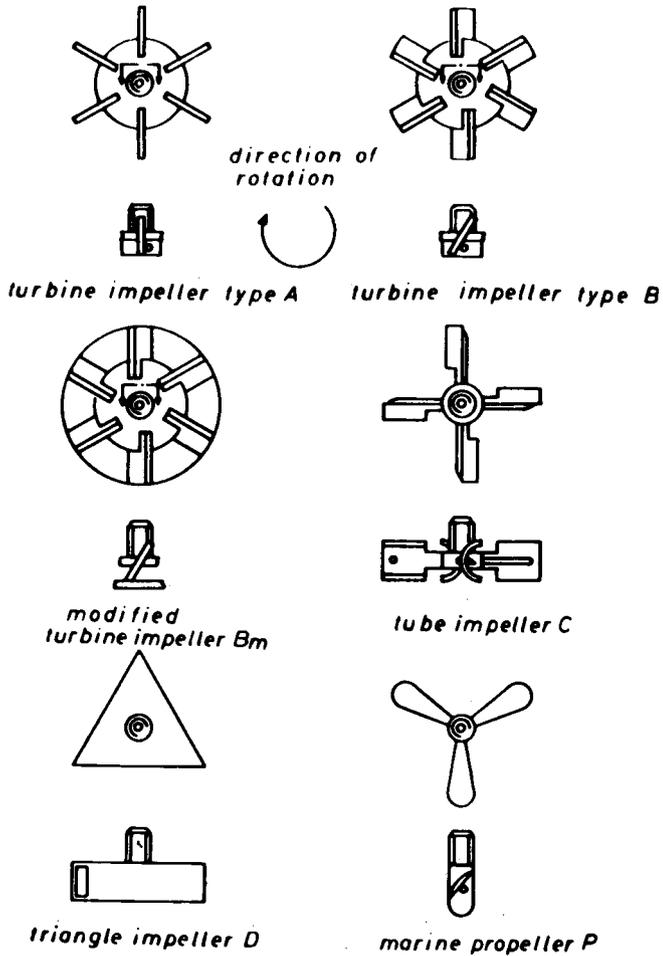


Fig. 4—Stirrer types

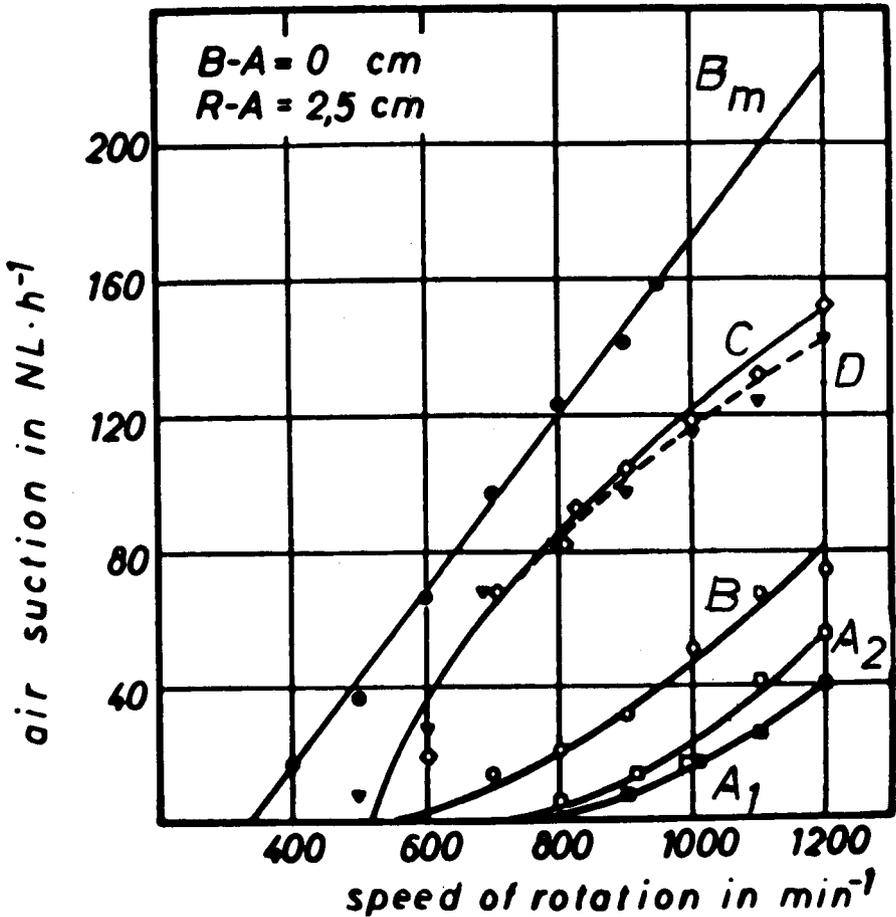


Fig. 5—Air suction as a function of speed of rotation

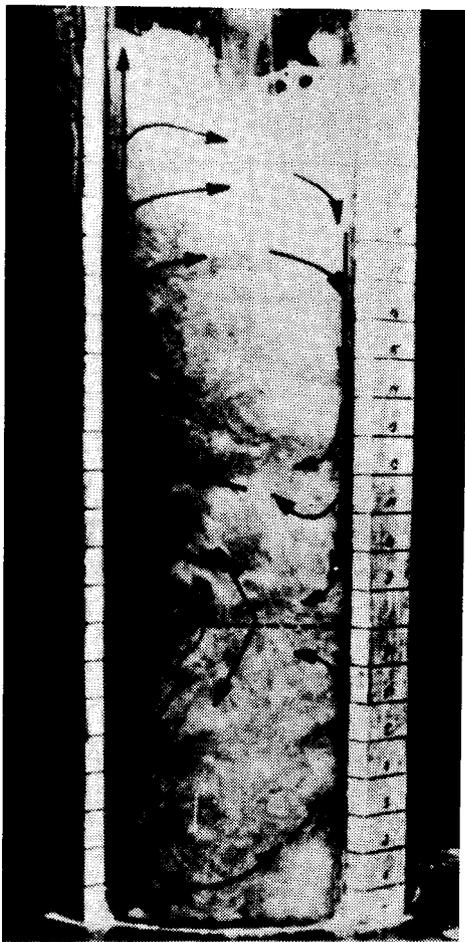


Fig. 6—Gas-liquid mixture in equipment

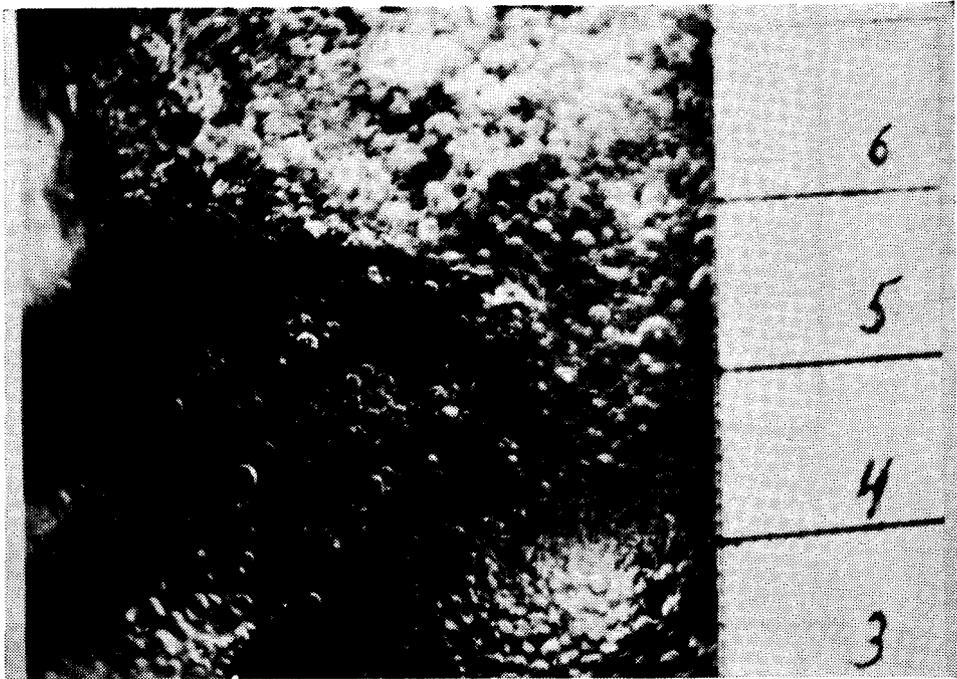


Fig. 7—Gas-liquid mixture in equipment

Two factors have to be considered for the transport of dissolved oxygen to the solid's surface: the degree of suspension of the solid and the blocking of the free reaction surface by gas bubbles. If the solid is completely suspended by the stirring effect, further increase of rotation speed has almost no more influence on the dissolution rate. The application of ultrasonics is only efficient, if the degree of suspension is not maximum, because then an additional suspension effect occurs, as shown in Fig. 9. The small effect of ca. 30 per cent increase of the dissolution rate can be explained by an additional movement of the particles caused by the ultrasonic energy.

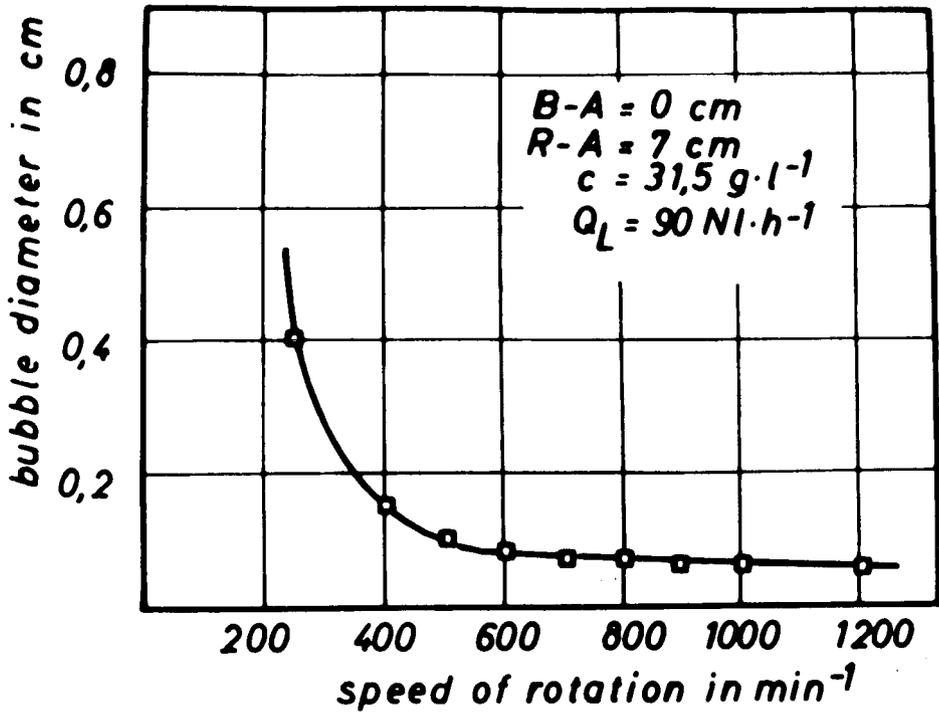


Fig. 8—Bubble size as a function of speed of rotation

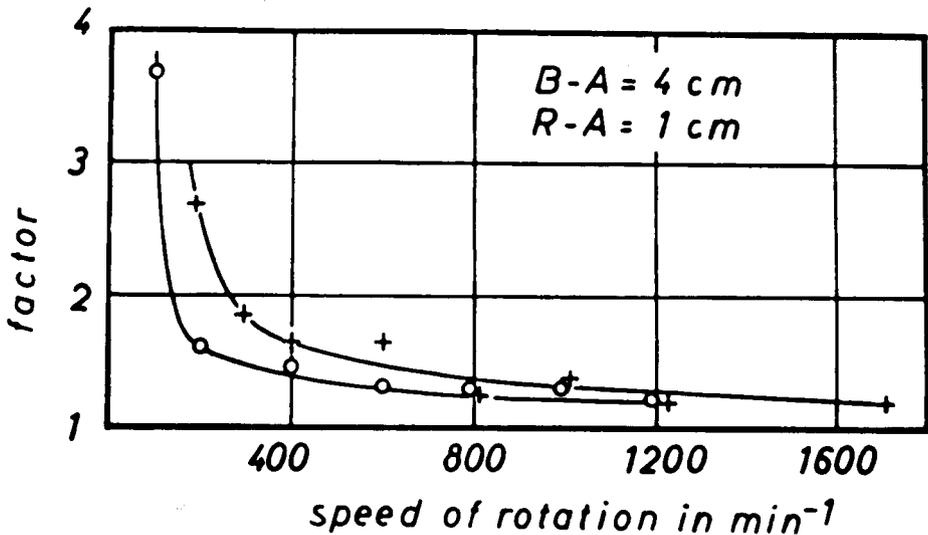


Fig. 9—Effect of ultrasonics as a function of speed of rotation

The effect of blocking of the surface by gas bubbles is shown in Fig. 10, where leaching of  $\text{Cu}_3\text{As}$  was carried out at a constant rotation speed, but with increasing amounts of  $\text{O}_2$ . With increasing amounts of oxygen under the chosen conditions, there is an increase in the rate of dissolution up to a value of 70 normal litres per hour, after which there is a decrease caused by surface blocking by gas bubbles. The efficiency of utilization of the oxygen is also strongly decreased, because instead of many small bubbles just a few big ones with a smaller surface area are formed.

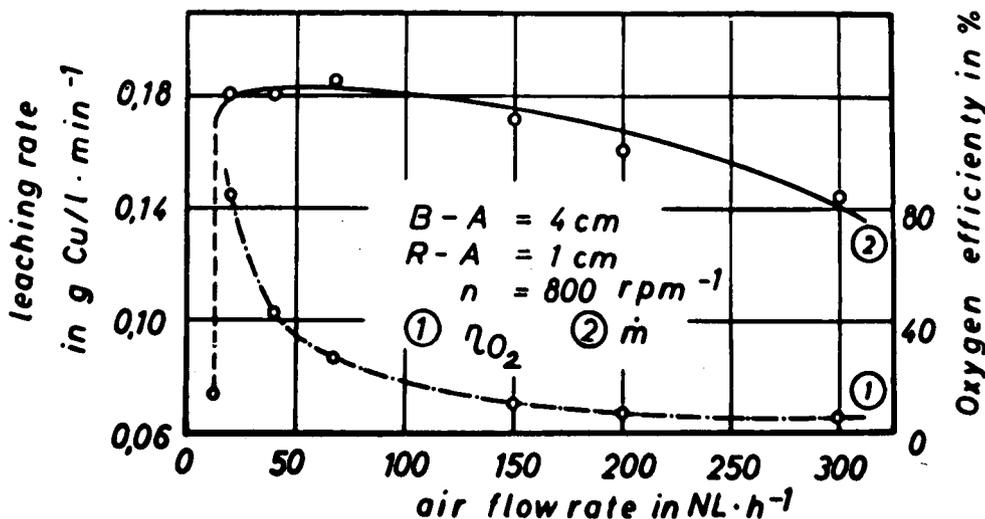
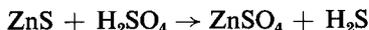


Fig. 10—Leaching rate and oxygen efficiency as a function of the air flowrate

Under ideal conditions and with certain assumptions, such as the perfect spherical shape of the gas bubbles and the closest packing of spheres, one can calculate, that the time spent in the liquid is approximately 13 sec and that their average ascension speed is about 1.1 cm/sec.

For the investigation of events at the phase boundary, a mineral was chosen, which had the simplest possible composition. This was a very pure blende from Spain with 67.0 per cent Zn, 31.6 per cent S, 0.6 per cent Cu, and no iron or other heavy metals. The experiments<sup>16</sup> were first carried out under the technical conditions of 110°C, 10 atm  $\text{O}_2$ -pressure for a two hour period. It was a disappointment to find out, that only 12 per cent of the theoretically possible amount had dissolved under these conditions.

It was shown in all experiments, that  $\text{H}_2\text{S}$  was formed from the beginning, so that one may with certainty assume, that the first reaction is



One can also imagine this as an electrochemical reaction and thereby assume the following scheme (Fig. 11).

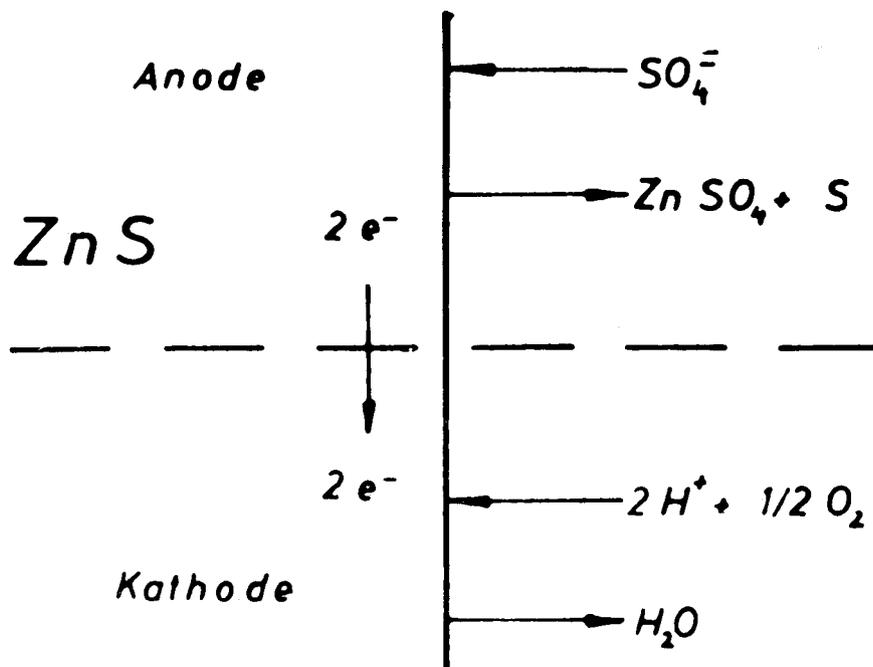


Fig. 11—Electrochemical model of the dissolution of ZnS

In this scheme it is mandatory, that electron transport can take place in the solid. Zinblend is a semi-conductor and so at room temperature it is almost an insulator. Its specific resistance was found to be  $6 \times 10^9 \Omega \text{cm}$  at  $90^\circ\text{C}$ . Before a reaction on the surface of the solid can take place, oxygen molecules from the solution must be adsorbed. The reacting gas is bound to the surface by mutual exchange or by electron exchange. A theory of boundary chemisorption has been developed to explain these events. According to this theory, the number of charge carriers in the semiconductor can be enlarged by the presence of foreign atoms (electron donors), by the addition of extra chemical substances to the solution (Redox-systems), or by the raising of electrons from the valence band to the conductivity band by means of irradiation.

The influence of UV was first studied. It was necessary to work at a pressure of 1 atm and at  $70^\circ\text{C}$  because of technical limitations. The results are shown in Fig. 12. With pure ZnS, the energy difference between the valence band and the conductivity band is so large, that the UV irradiation cannot span the difference, only after doping can this be achieved. The reaction results are in agreement with this: pure ZnS does not react to UV irradiation, while doped ZnS shows a considerable increase in solubility.

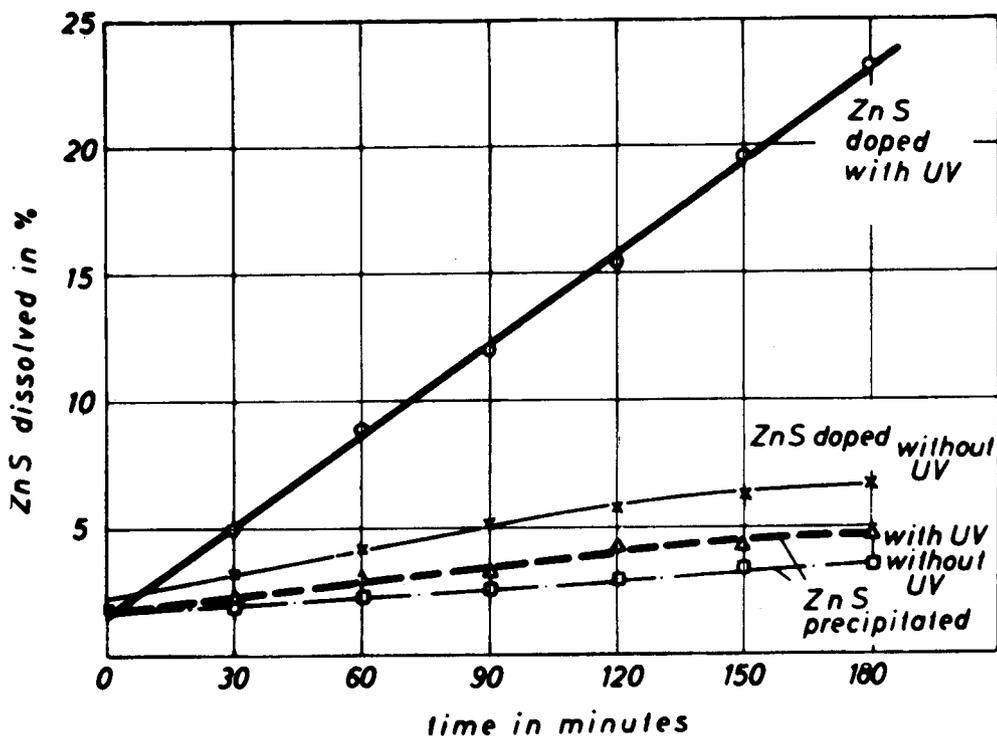


Fig. 12—Influence of UV on the dissolution of ZnS

Electrons can also be supplied by a Redox system. In this experiment the Redox system was formed by the addition of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{I}_2$ ,  $\text{Ti}^{3+}$  and  $\text{Ce}^{4+}$ . The expected result for iron is demonstrated in Fig. 13. The addition of an amount of  $\text{Fe}^{3+}$  corresponding to 10 per cent of the total weight of the used zincblende results in a five-fold increase in the dissolution rate. The addition of copper shows a weak influence, while all other additions were either destroyed or precipitated by  $\text{H}_2\text{S}$ .

Fig. 14 shows, that concentrates of zincblende contain varying amounts of iron. The extraction values correspond with one exception to the iron content of the concentrates. Both of the concentrates with more than 10 per cent iron were investigated by means of X-ray analysis, which showed, that the poorly soluble concentrates contained the iron as a solid solution, while the highly soluble concentrates contained the iron in the form of pyrites or pyrrhotites. This indicates, that Fe is not effective as a donor in the zincblende lattice.

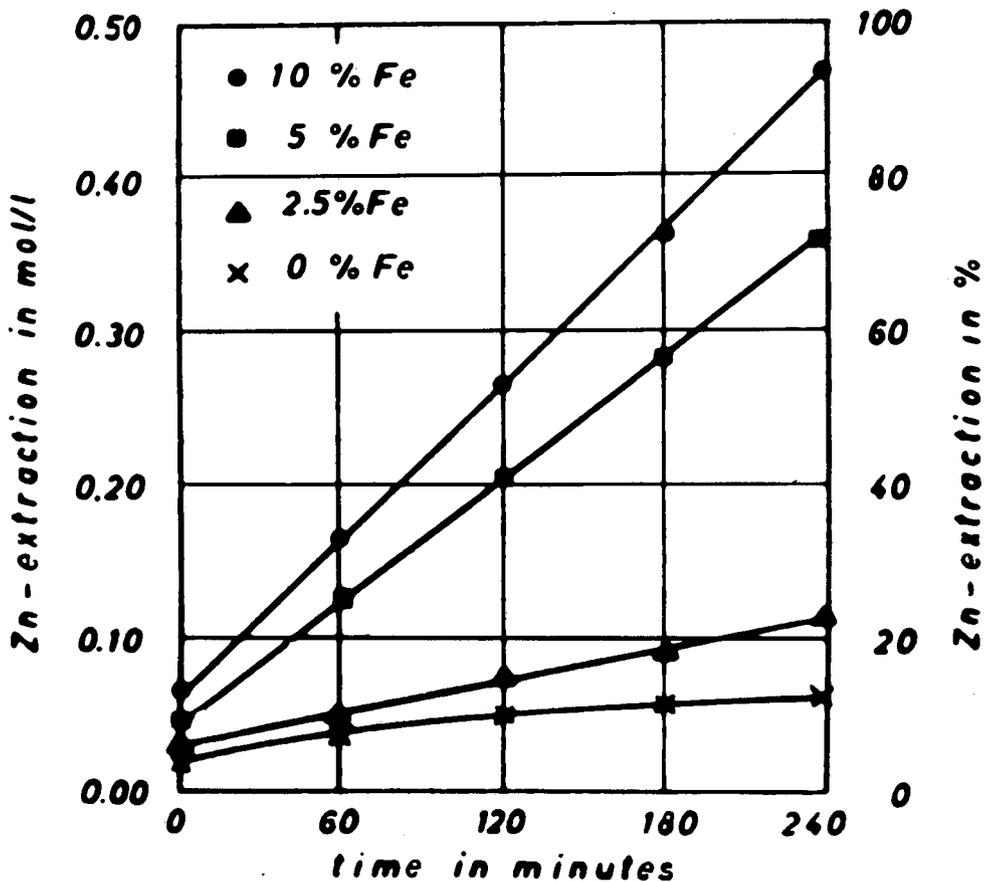
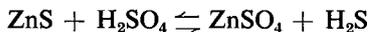


Fig. 13—Influence of Fe on the dissolution of ZnS

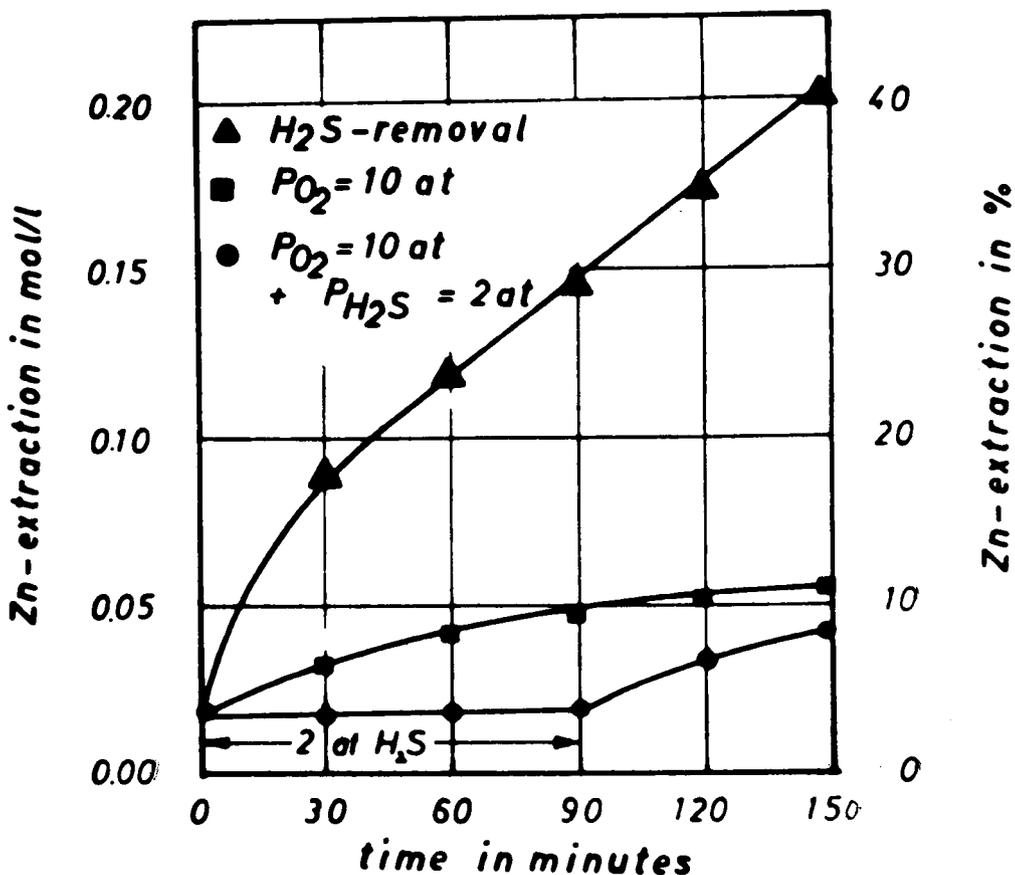
Concentrate	Analysis		CaO %	Fe diss. %	Zn diss. %	Cu%
	Zn%	Fe%				
Prealpina	58,8	0,7	3,0	---	14,5	0,17
Minerva	60,5	2,25	1,6	33,1	17,5	0,08
Gailitz	58,3	2,42	2,68	38,9	16,8	0,12
Pyhäsalmi	54,9	8,3		41,7	36,0	0,33
Kassandra	52,7	8,5		24,2	38,0	0,84
Meggen	47,0	10,0		52,0	65,2	0,10
Cartagena	54,75	10,25		43,4	23,0	0,51
Brunswick	49,5	11,8		28,8	72,3	0,10

Fig. 14—Analysis of zincblende concentrates

However, it was found that sulfides with a considerably higher electric conductivity by no means dissolved faster than the poor semi-conductor ZnS. There must therefore be still another factor hindering dissolution. This was found to be the H<sub>2</sub>S which is formed during the leaching. Fig. 15 shows, that the continual removal of H<sub>2</sub>S can increase the leaching rate approximately 4-fold, while adding H<sub>2</sub>S at a pressure of 2 atm can completely suppress the reaction. This is due to the fact, that an equilibrium occurs in the reaction



This equilibrium brings the reaction to a stop. From the approximate data in the above mentioned case, an equilibrium pressure of ca 0.5 atm H<sub>2</sub>S can be calculated, which agrees well with the experimental results. The removal of H<sub>2</sub>S can in principle be accomplished according to the equations in Fig. 16. The first reaction takes place only at very high concentrations of H<sub>2</sub>SO<sub>4</sub>, the third reaction apparently takes place only at very high temperatures. The middle reaction takes place only very slowly, and the problem is to accelerate it. It has been known for a long time, that oxidation reactions can be accelerated by activated carbon. This has been used successfully for the oxidation of H<sub>2</sub>S to S°. Fig. 17 shows that activated carbon can increase the oxidation of H<sub>2</sub>S and thereby the leaching rate of zincblende by a factor of approx. 5.

Fig. 15—Influence of  $H_2S$  on the dissolution of  $ZnS$ Fig. 16—Possible oxidation reactions for  $H_2S$

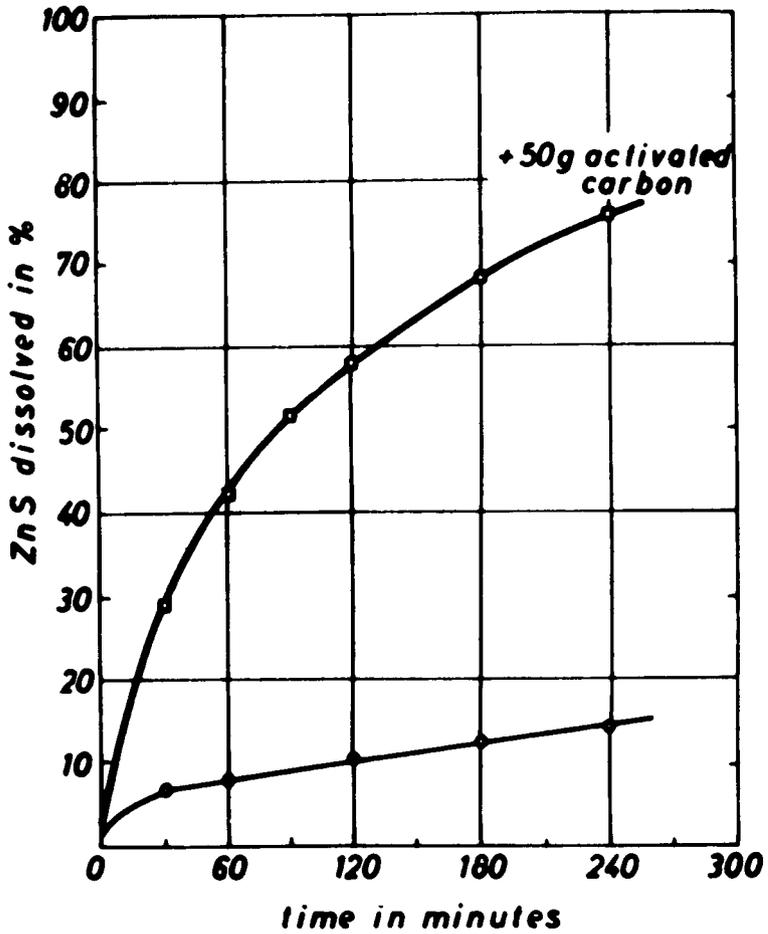


Fig. 17—Influence of activated carbon on the dissolution of ZnS

As shown in Fig. 18, the leaching rate of most of the other sulfides is also strongly influenced by the oxidation rate of  $H_2S$ , but at the same time one has to conclude, that there must be a third factor of importance besides the electric conductivity and the acceleration of the oxidation of  $H_2S$ , namely the atomic structure of the components. Fig. 19 shows an attempt to co-ordinate the atomic structure, the co-ordination number and the electrical resistance. However, it is not convincing, because we still know too little about the atomic bonding conditions, especially about the relative proportions of covalent and ionic bonds. It is striking, that the leaching of chalcopyrite ( $CuFeS_2$ ) is exceptionally difficult<sup>17</sup>. Economical leaching is only possible by either destroying the structure by means of heating and distilling part of the sulphur away or by the reaction with cement copper. At temperatures of more than  $160^\circ C$  the dissolution apparently occurs by quite a different mechanism. Fig. 20 shows that a great increase of the dissolution rate occurs above this temperature and that, instead of the primarily formed  $H_2S$ , now  $SO_4^{2-}$  arises. A stepwise oxidation of the  $H_2S$  through  $S^\circ$  to  $SO_4^{2-}$  can be excluded because of the very slow second step. There are no explanations yet for this phenomenon.

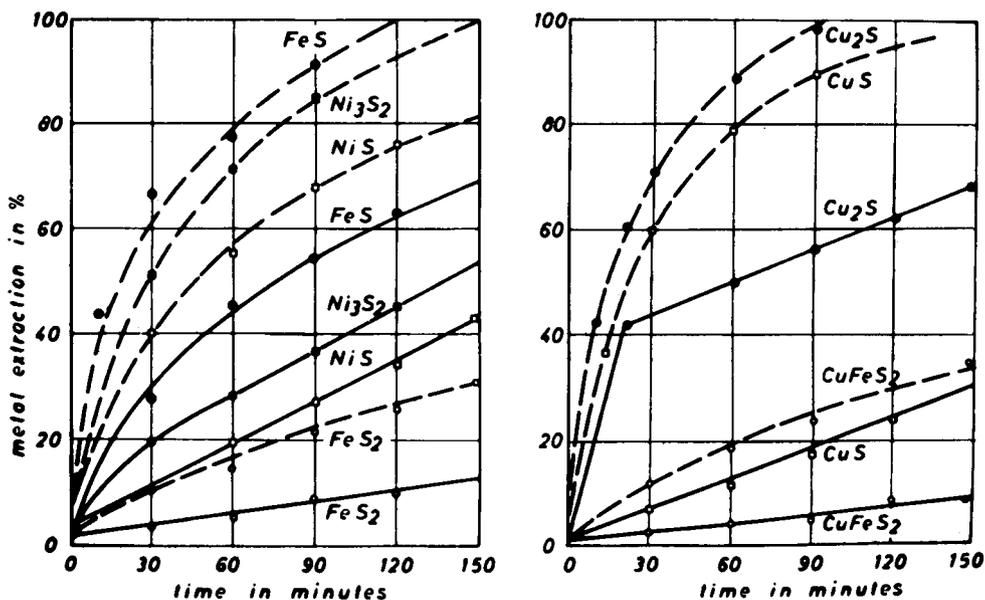


Fig. 18—Leaching rate of different metal-sulphides

**Data of Dissolution and Resistivities**

temperature: 90°C      time: 1 hour

coordination number	4		4/6			6			12			
	resistivity $\rho$ ( $\Omega\text{cm}$ )	dissolution %		g	%		g	%		g	%	
ZnS	$6 \cdot 10^9$	7	Ni <sub>3</sub> S <sub>2</sub>	$9 \cdot 10^{-2}$	30		PbS	$5 \cdot 10^1$	25	Cu <sub>3</sub> As	$6 \cdot 10^{-2}$	100
ZnSe	$1,5 \cdot 10^7$	25	CuS	$1 \cdot 10^{-1}$	20		FeS	$2 \cdot 10^1$	100			
ZnTe	$2,7 \cdot 10^4$	100					NiS	$2 \cdot 10^{-1}$	18			
ZnS	$6 \cdot 10^9$	7				As-S	CoAsS	$6 \cdot 10^0$	26			
Cu <sub>2</sub> FeSnS <sub>4</sub>	$1 \cdot 10^2$	24				S-S	FeS <sub>2</sub>	$10^0$	36			
CuFeS <sub>2</sub>	$3 \cdot 10^1$	5				As-S	FeAsS	$10^0$	38			
Cu <sub>3</sub> SbS <sub>4</sub>	$7 \cdot 10^0$	10				stat.	NiAsS	$5 \cdot 10^{-2}$	39			
						Sb-S	NiSbS	$2 \cdot 10^2$	66			

Fig. 19—Data of dissolution and resistivities

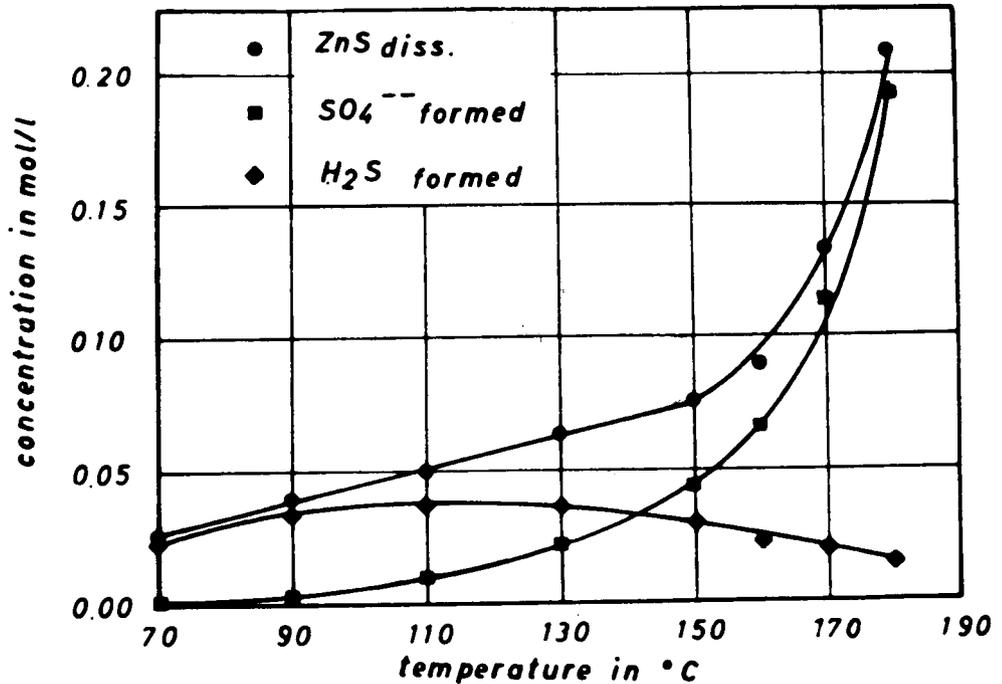


Fig. 20—Influence of temperature on the reaction occurring at the leaching of ZnS

The last step in the leaching process is the removal of reaction products from the surface of the solid. In this regard it is important to consider, that the solubility of the sulfate formed decreases greatly at high temperatures<sup>18</sup> (Fig. 21). In particular,  $\text{FeSO}_4$  is already completely insoluble at  $160^\circ\text{C}$ .

Finally, two examples of the use of pressure leaching for the processing of smelter by-products will be described<sup>19</sup>.

During the processing of copper dross in lead refining, a lead-copper-matte is formed. Its composition and leachability at  $100^\circ\text{C}$  and 10 atm  $\text{O}_2$  is shown in Fig. 22. The X-ray analysis of the matte indicates  $\text{ZnS}$ ,  $\text{PbS}$  and  $\text{CuFeS}_{2-x}$ . The residue of the leaching process consists of  $\text{PbSO}_4$  and  $\text{S}^\circ$  in addition to small particles of undissolved matte. In Fig. 23 a possible flow sheet is presented.

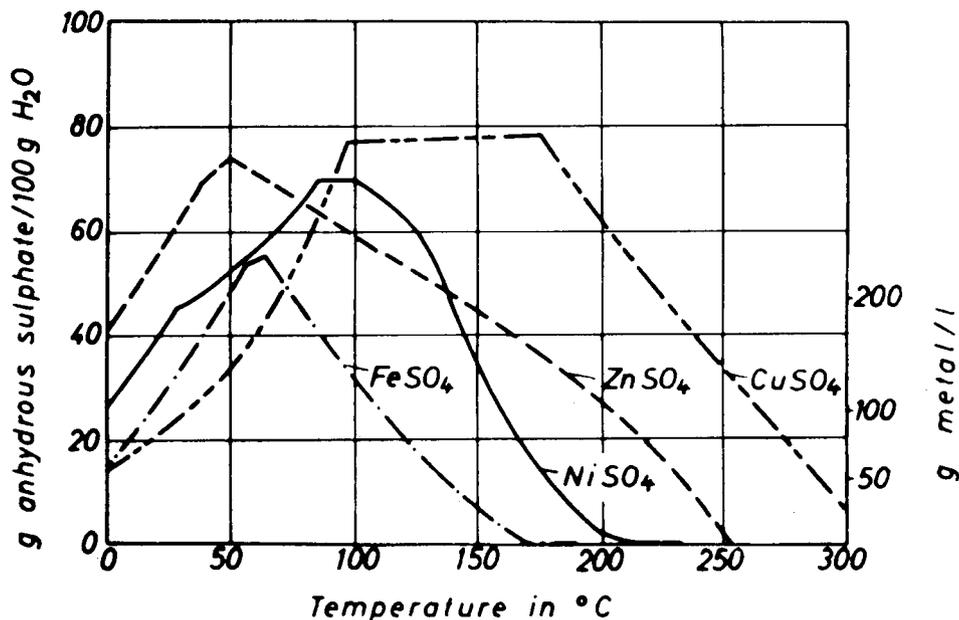


Fig. 21—Solubility of some metal-sulphates as a function of temperature

**Pressure leaching of Cu-Pb-Matte D 9**

**Analysis** Cu:32,2%, Pb:26,5%, Fe:11,2%, S:18,8%  
**Conditions:**  $H_2SO_4=60$  g/l,  $PO_2=10$  at,  $T=100^\circ$  C  
 solid:liquid = 1:20  
 material <  $60 \mu m$

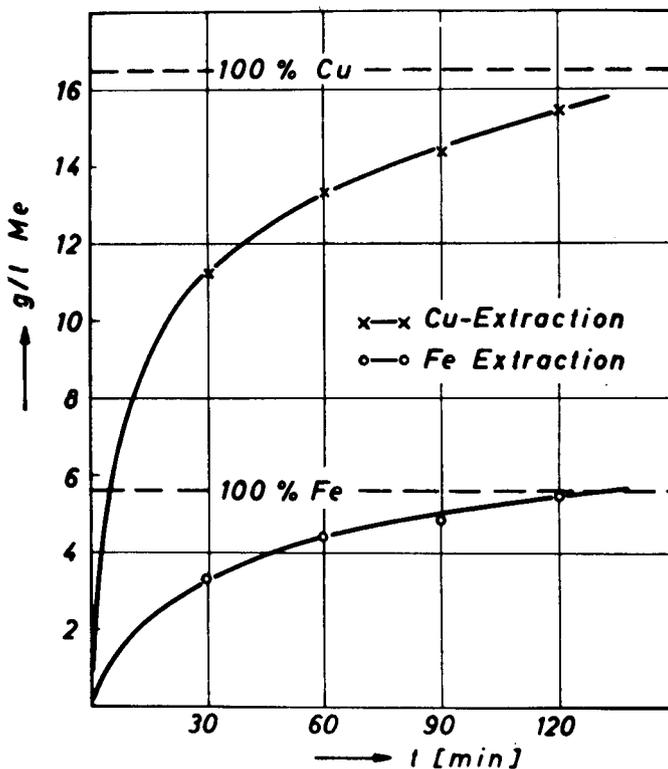


Fig. 22—Pressure leaching of Cu-Pb-matte

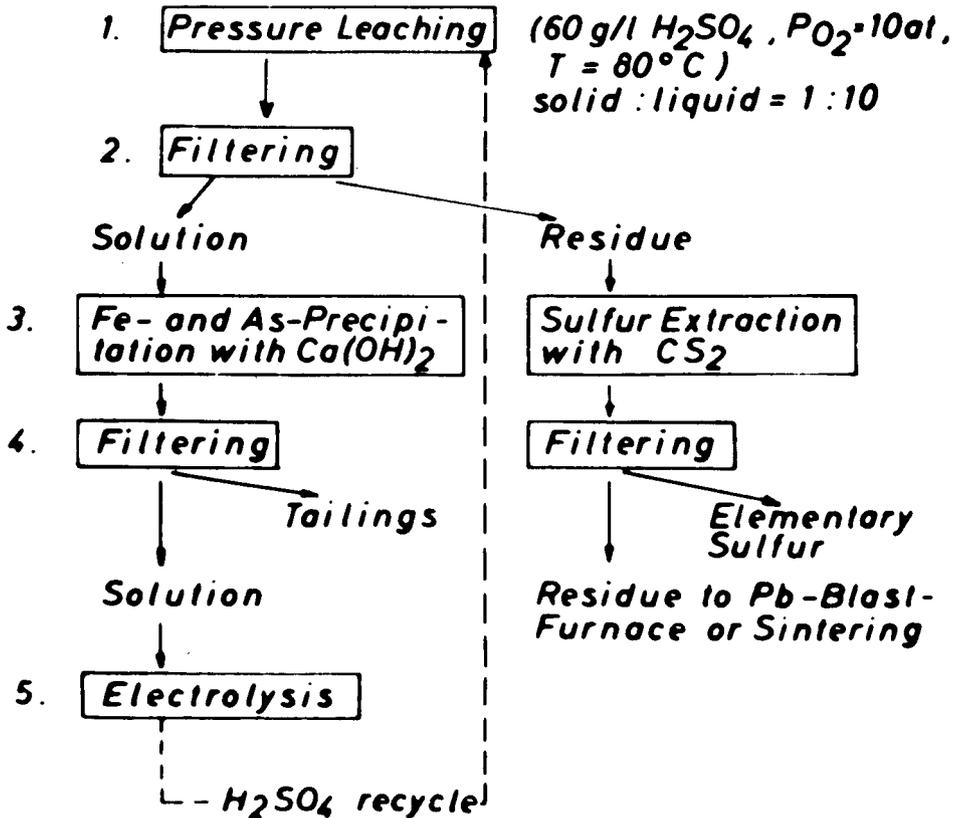
Hydrometallurgical Treatment of Cu-Pb-Matte

Fig. 23—Hydrometallurgical treatment of Cu-Pb-matte

Finally, speisses, as they occur in lead smelting, have been subjected to pressure leaching. The compounds shown in Fig. 24 were found to be components of the speisses by means of X-rays<sup>20, 21, 22</sup>. In model experiments it was shown, that arsenides go into solution much easier than sulfides. NiAs, for instance, is completely dissolved under much milder conditions, such as two hours at 60°C and 1 atm  $O_2$ . The problem in processing speiss is the removal of arsenic. Since arsenic is oxidized to  $HAsO_4^{2-}$  by pressure leaching in alkaline solutions and since this compound can be easily converted into an insoluble substance, alkaline leaching was also investigated. A summary of the components of speiss and the yield of the most important substances after the different leaching processes is given in Fig. 25. The acid leaching has an advantage, because on account of the mild leaching conditions all the noble

metals in heavy decomposable sulfides remain as such in the residue and can be separated from the lighter sulfates and basic salts of Pb, Sb and Sn in a hydrocyclone. The sulfides go to a copper smelter, the sulfates of the residue to a lead smelter and the leaching solution can be separated from arsenic by means of concentration by evaporation (Fig. 26).

With ammoniacal leaching there is the disadvantage, that a distribution of silver between the solution and the residue occurs. Therefore it is not recommended, pending further study.

At the end I would like to thank the "Deutsche Forschungsgemeinschaft", the Senator of Economics in Berlin and the Federal Ministry of Economics for sponsoring these investigations.

### Constituents of Speisses

<b>Metals</b>	<b>Cu, Pb</b>	<b>Ag, Au</b>
<b>Sulfides</b>	<b>Cu<sub>2</sub>S, FeS, PbS</b>	
<b>Arsenides</b>	<b>NiAs, Ni<sub>5</sub>As<sub>2</sub>, Ni<sub>11</sub>As<sub>8</sub>, FeAs, Fe<sub>2</sub>As, Cu<sub>3</sub>As</b>	<b>Sb, Sn, Co</b>

Fig. 24—Constituents of speisses

### Pressure Leaching of Speiss 127 in H<sub>2</sub>SO<sub>4</sub>, NH<sub>3</sub> + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NaOH

*P*O<sub>2</sub> = 10 at, *T* = 80° C, *t* = 120 min, 100 g/l Speiss

H<sub>2</sub>SO<sub>4</sub> = ca. 2,45 mol/l

NH<sub>3</sub> = ca. 5,8 mol/l + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = 1,5 mol/l

NaOH = ca. 2,5 mol/l

Element	H <sub>2</sub> SO <sub>4</sub>	NH <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	NaOH	Contents of Speiss 127
Cu	100,0 %	92,5 %	1,8 %	25,9 %
Ni	100,0 %	81,9 %	-	10,9 %
Co	100,0 %	n. d.	-	2,7 %
As	65,0 %	53,8 %	23,8 %	27,7 %
Pb	-	n. d.	81,0 %	15,7 %

Fig. 25—Pressure leaching of speiss

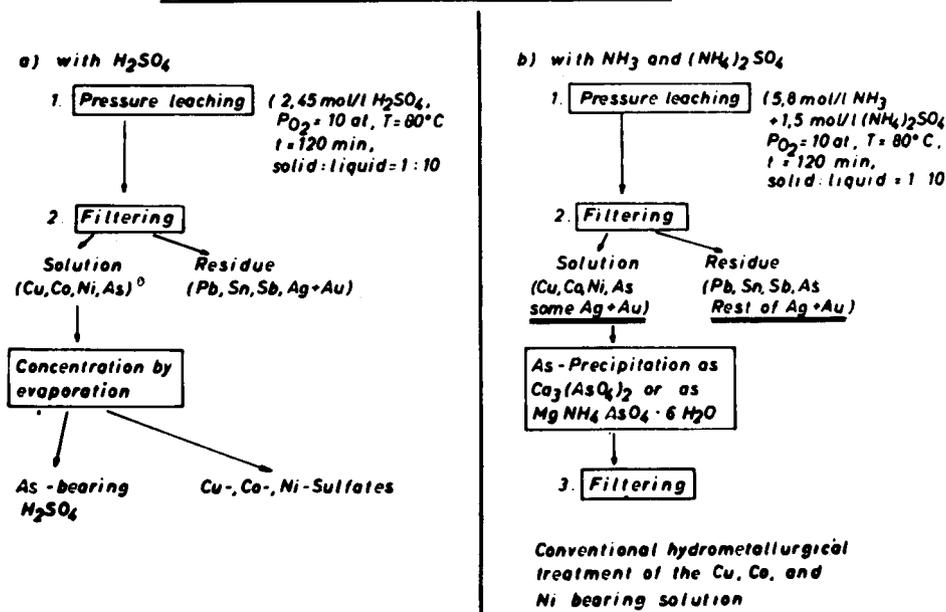
**Hydrometallurgical Treatment of Spieisses**

Fig. 26—Hydrometallurgical treatment of spieisses

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