

## Recent developments for the removal of arsenic and antimony from processing waters of the glass industry<sup>1)</sup>

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Since 1990 the concentrations of arsenic and antimony in waste waters of the glass industry have been limited in the Federal Republic of Germany. Lead crystal, crystal, and a lot of special glasses contain arsenic and/or antimony which enter the processing waters when the glasses are ground or treated by acid polishing. Therefore, these waters have to be cleaned before entering the drainage ditch.

Grinding waters can be recycled by the precipitation of arsenic and antimony by ferric ions, the precipitate being separated together with the glass abrasion products. In processing waters from the acid-polishing process, however, arsenic and antimony partly form fluorocomplexes which cannot be precipitated by ferric ions. A new waste-water treatment by quaternary ammonium ions which precipitate hexafluoroarsenate – in addition to existing neutralization equipments – will meet the new regulations.

### Neue Entwicklungen der Abreinigung von Arsen und Antimon aus Betriebswässern der Glasindustrie

Seit 1990 gelten in der Bundesrepublik Deutschland Konzentrationsgrenzwerte für Arsen und Antimon im Abwasser der Glasindustrie. Bleikristall- und Kristallgläser sowie eine Vielzahl Spezialgläser enthalten Arsen und/oder Antimon, das beim Schleifen oder bei der Säurepolitur der Gläser in die Betriebswässer gelangt. Daher muß man diese Wässer reinigen, bevor sie in den Vorfluter geleitet werden.

Schleifereiwässer können im Kreislauf geführt werden, indem man Arsen und Antimon durch Zugabe von Eisenionen ausfällt und zusammen mit dem Glasabrieb abtrennt. In den Prozeßbädern der Säurepolitur bilden Arsen und Antimon jedoch teilweise Fluorokomplexe, die nicht durch Eisenionen ausfällbar sind. Mit einer neuen Abwasserbehandlungsmethode, in Kombination mit existierenden Neutralisationsanlagen, lassen sich Hexafluoroarsenate durch Zugabe von quaternären Ammoniumsalzen ausfällen und somit die neuen Umweltschutzbestimmungen sicher einhalten.

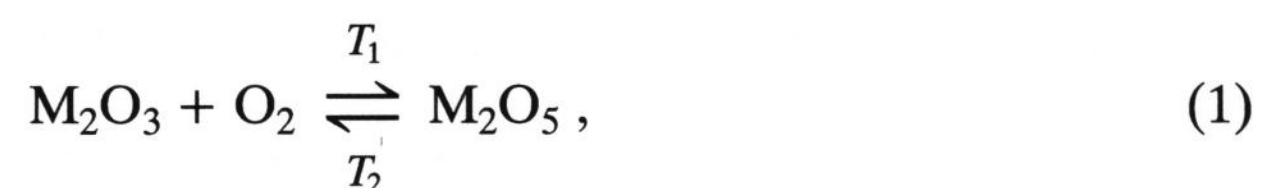
## 1. Introduction

According to an inquiry made in 1986, the German glass industry uses 145 t  $\text{As}_2\text{O}_3$  per year as a fining or decolourizing agent [1] and is thus one of the most important consumers of arsenic in the Federal Republic of Germany. Since it is well-known that arsenic is very carcinogenic and toxic – the lethal dose by oral application amounts from 1.0 to 2.5 mg/kg body weight [2] – many attempts have been made to substitute it. Up to now no other adequate reagent has been found for fining lead crystal, crystal, and a lot of special glasses but antimony [3], which is very similar to arsenic in its toxicity [4]. As long as both elements are fixed in the glass matrix, there is no danger for the environment. Those portions of arsenic and antimony, however, which are carried off when the glasses are ground or treated by acid polishing are dissolved to a great deal and might enter the waste water.

Since 1990 a new regulation for the protection of the environment has become valid in the Federal Republic of Germany [5], in which the concentrations of arsenic and antimony in grinding waters are limited to  $< 0.3$  mg/l. Additionally, a freight limit for arsenic has been established for waste water of the acid-polishing process. Antimony is not yet limited in this regulation, but generally the administration will take the same freight limit as for arsenic. To stay within these limits, now, many German glassworks have to take means to remove arsenic and antimony from processing waters.

## 2. Input and whereabouts of arsenic and antimony in the glass-making process

Arsenic and antimony are used as fining agents mostly in form of  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$ . Both compounds are able to bind oxygen at a rather low temperature  $T_1$  and release it at a higher temperature  $T_2$ :



with  $\text{M}$  = arsenic or antimony and  $T_1 < T_2$ .

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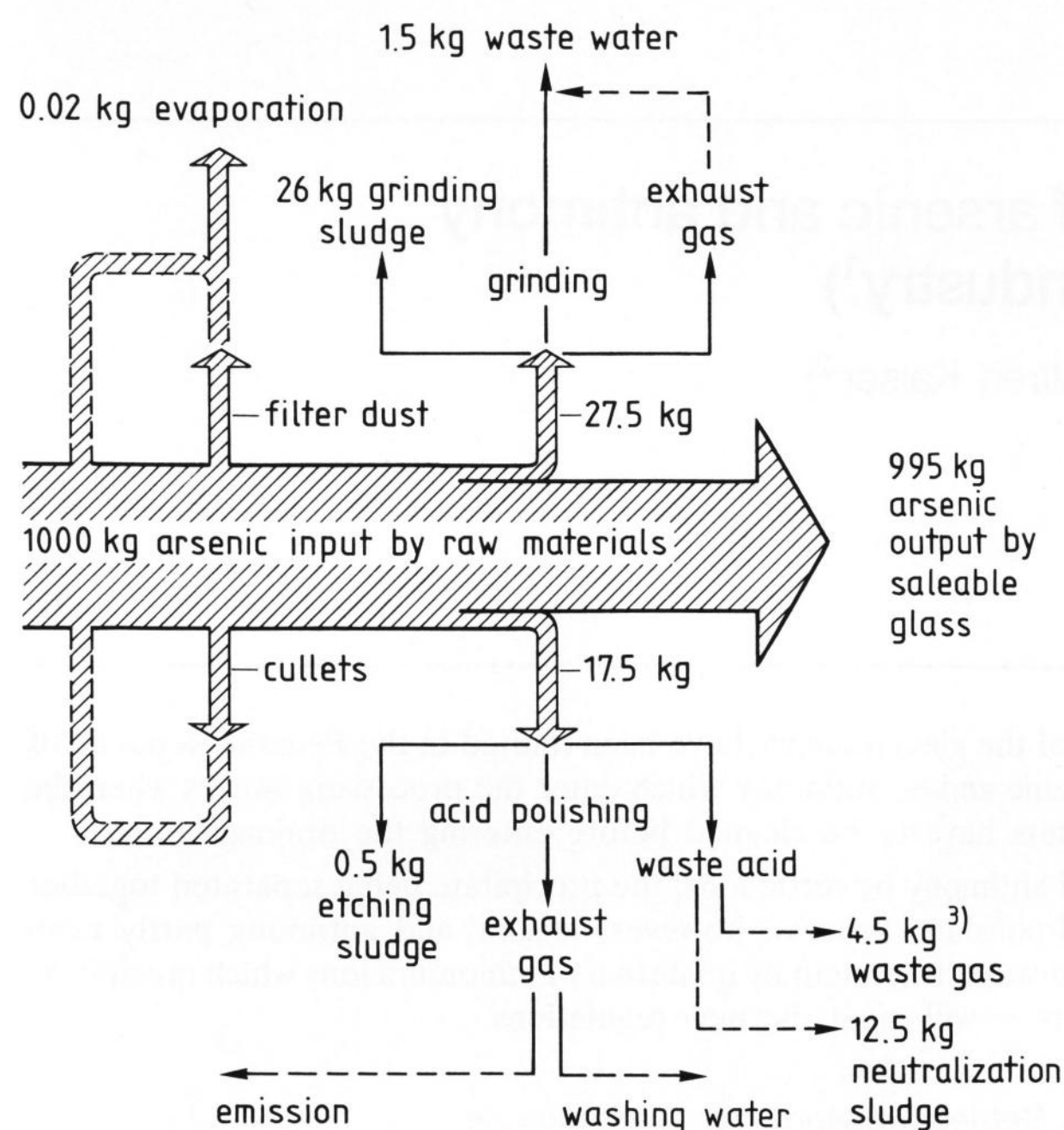


Figure 1. Mass flow of arsenic within a glassworks producing lead crystal glasses.

<sup>3)</sup> Including the amount of exhaust gas washing water.

By the release of oxygen, bubbles are formed which ascend to the surface of the glass melt taking along other small gas bubbles. The aim of this "chemical" fining process is to homogenize the melt and to free it from gaseous inclusions.

Under working conditions it is necessary to use about two times more  $Sb_2O_3$  than  $As_2O_3$  by weight to obtain the same fining result. Since  $Sb_2O_3$  is more expensive (5.50 DM/kg) than  $As_2O_3$  (2.00 DM/kg), nowadays most glassworks use  $As_2O_3$ ; only a few carry out a pure  $Sb_2O_3$  or a combined  $As_2O_3/Sb_2O_3$  fining. But new developments in the field of melting process, e.g. electrical melters [6] and the so-called Crisver<sup>®</sup> process [7], will increase the  $Sb_2O_3$  consumption. One reason for these new developments is the lower fining temperature which can be achieved by the use of  $Sb_2O_3$  leading to lower melting energy consumption. The release of oxygen starts in the case of  $Sb_2O_3$  at temperatures between 70 and 100 K lower than with  $As_2O_3$  [8].

Lead crystal and crystal glass batches normally contain up to 0.2 wt%  $As_2O_3$  and up to 0.4 wt%  $Sb_2O_3$ . The respective concentrations in special glasses vary in a great range. But this production contributes only to a rather small extend to water pollution.

Figure 1 shows the main arsenic mass flows within a glassworks producing lead crystal glasses which are ground and treated by acid polishing. Comparable conditions are valid for antimony, too. The data presented are based on information given by ten

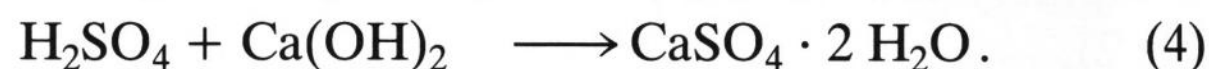
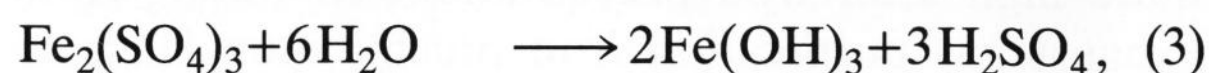
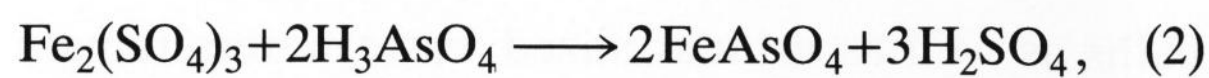
glassworks. The means of the individual values were normalized to 1000 kg arsenic input to the batch. The questioned glassworks recycle their own cullets exclusively. This practice is very common for the German lead glass industry. Moreover, in this scheme it is assumed that the filter dust from the melting process is completely recycled so that its arsenic content has not to be considered with respect to the mass balance. Nowadays about 30 wt% of the filter dusts from the lead glass production in Germany are directly remelted [9]; but another 30 wt% could possibly be recycled, too, so that the assumption of complete remelting may be justified.

Under these premises more than 95 wt% of the arsenic input remains in the saleable glasses (figure 1) and thus does not affect the environment. A rather small amount of arsenic (20 ppm) is lost during the melting process by evaporation and cannot be separated within the filter dust. There are two other ways, namely grinding and acid-polishing processes, on which arsenic ( $\approx 4.5$  wt%) leaves the glassworks dispersed in sludges and waste waters. In sections 3. and 4. investigations concerning the removal of arsenic and antimony from waste waters of grinding and acid-polishing processes are described in detail.

### 3. Removal of arsenic and antimony from grinding waters

Lead crystal glasses are frequently adorned by cuts and grindings. By these decoration processes up to 10 % of the glass is mechanically carried off in form of very small particles. Since these particles have large specific surface areas, they can easily be leached by water in which heavy metals like lead, arsenic, and antimony are dissolved. Cooling waters from lead crystal glass grinders contain up to 10 mg lead/l and up to 3 mg arsenic/l and antimony, respectively. Usually the antimony concentrations are smaller than the arsenic concentrations due to the lower solubility of antimony compounds. If the cooling water is recycled in order to reduce the water consumption, arsenic accumulations up to more than 10 mg/l are observed.

Whereas the precipitation of lead ions by  $CO_2$  has been used by the glass industry for several years [10], a technique for the removal of arsenic from waste waters was developed only three years ago [11 and 12]. It is based on the well-known precipitation of arsenates by  $Fe^{3+}$  ions which are separated together with the glass particles. As precipitation agents  $Fe_2(SO_4)_3$  and  $Ca(OH)_2$  are used. This combination avoids a decrease of the pH value as well as an increase of  $SO_4^{2-}$  ions in the water, since scarcely soluble  $CaSO_4 \cdot 2H_2O$  (gypsum) is formed. The overall reactions can be described by equations (2 to 4):



It was found that under working conditions there is no oxidation necessary to convert the  $\text{As}^{3+}$  to the  $\text{As}^{5+}$  ion, the latter forming less soluble compounds with iron than the  $\text{As}^{3+}$  ion. To achieve residual arsenic concentrations  $< 0.3 \text{ mg/l}$ , one has to use about a fiftyfold molar excess of  $\text{Fe}^{3+}$  ions compared to the arsenic content of the water.

Figure 2 shows a flow chart of a production scale equipment for the treatment of  $15 \text{ m}^3$  waste water per hour at which arsenic and lead precipitation facilities are combined. This equipment has been working since 1986 and is able to reduce the arsenic and lead contents of the grinding waters to  $< 0.3 \text{ mg/l}$  and  $< 0.5 \text{ mg/l}$ , respectively. The operation costs for this treatment require about  $0.1 \text{ DM/m}^3$  waste water. Recent developments showed that also antimony concentrations can reliably be decreased to  $< 0.3 \text{ mg/l}$  by this method. For small-scale plants ( $0.1$  to  $0.4 \text{ m}^3$  waste water/h throughput) the waste-water treatment can be simplified by using only one mixture of suitable solid precipitation reagents instead of four separate dose equipments [13]. Per cubic metre of treated water about  $2 \text{ kg}$  (dry mass) of sludge are produced. Today this sludge has to be disposed as a waste material; but possibilities are under research to use the grinding sludge as an additive in other processes, e.g. the production of bricks.

Nowadays the removal of arsenic and antimony from grinding waters of the lead glass industry to residual concentrations  $< 0.3 \text{ mg/l}$  by precipitation with  $\text{Fe}^{3+}$  ions as discussed is already a reliable state-of-the-art technique. It can be combined with lead ion precipitation by  $\text{CO}_2$  without problems and its practical suitability was proven in large-scale applications as well as in small-scale plants.

#### 4. Removal of arsenic and antimony from waste waters of the acid-polishing process

In acid-polishing plants of the lead glass industry four different types of waste water occur: spent acid from the polishing bath, washing waters from cleaning the glassware and from exhaust gas purification, and neutralization waters. Table 1 gives their arsenic and antimony contents.

Polishing baths contain 60 to 70 wt%  $\text{H}_2\text{SO}_4$ , 0.5 to 10 wt%  $\text{HF}$ , and water. By moving the glasses in this mixture at temperatures between 30 and  $75 \text{ }^\circ\text{C}$  they are "chemically" polished. Thereby up to 10 % of the glass mass is dissolved. The components from the dissolved glass matrix react with the acids of the polishing bath to form lead sulphate ( $\text{PbSO}_4$ ) and

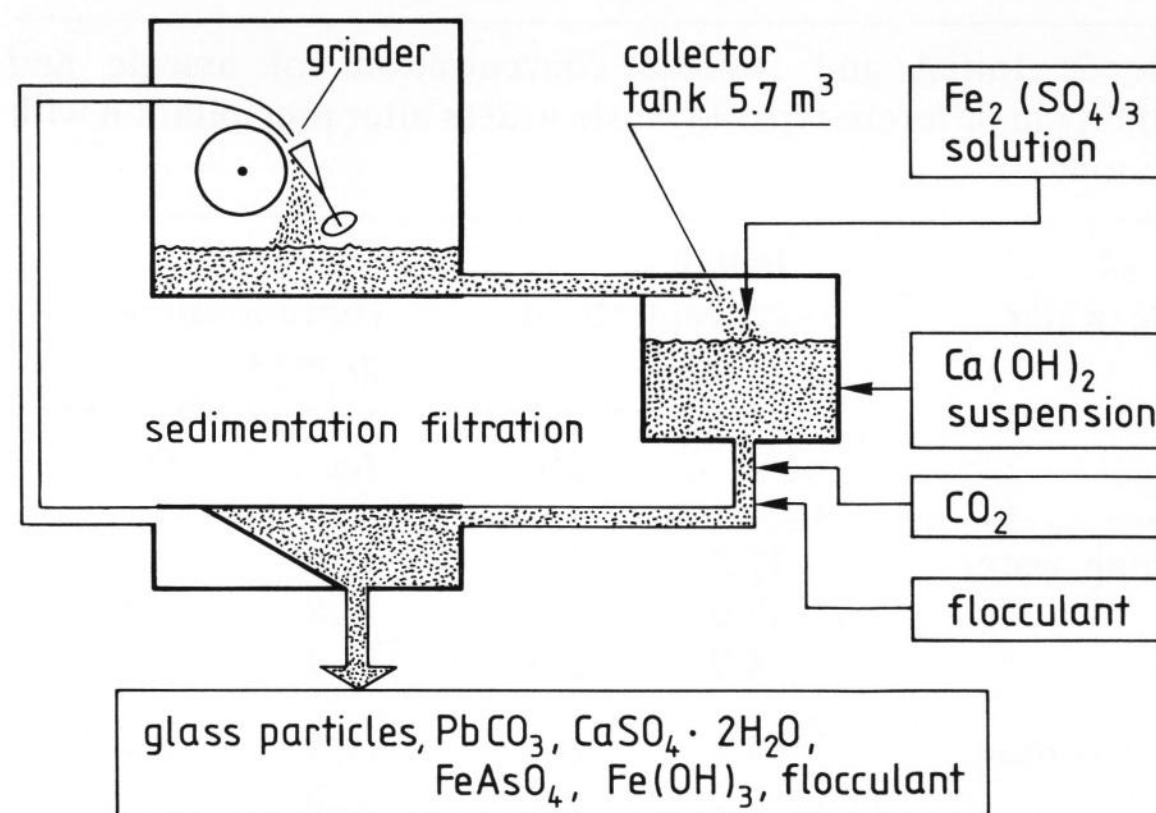


Figure 2. Flow chart of a production scale equipment for the removal of arsenic, antimony and lead from grinding waters.

Table 1. Arsenic and antimony concentrations in different types of waste waters from acid-polishing processes

type of waste water	concentrations in mg/l	
	As	Sb
waste acid	300 to 460	300 to 460
washing water	5 to 100	1 to 50
neutralization water	2 to 100	1 to 50
exhaust gas rinsing water	10 to 120	n. a.

n. a.: not analysed.

alkaline hexafluorosilicates (especially  $\text{K}_2\text{SiF}_6$ ). Both are scarcely soluble and can be separated as so-called etching sludge by filtration. Arsenic and antimony, however, remain in solution. Whereas both elements are dissolved in grinding waters only as oxoanions, they partly form complexes of hexafluoroarsenate ( $\text{AsF}_6^-$ )<sup>4</sup> and hexafluoroantimonate ( $\text{SbF}_6^-$ ) in the  $\text{HF}$ -containing polishing baths [14]:



with  $\text{M}$  = arsenic or antimony.

The fluoro complexes also enter the washing baths and are even found in waste waters after neutralization. In rinsing waters from wet air scrubbers, where arsenic gets to by transport through the gas phase, however, the hexafluoro complexes were not identified.

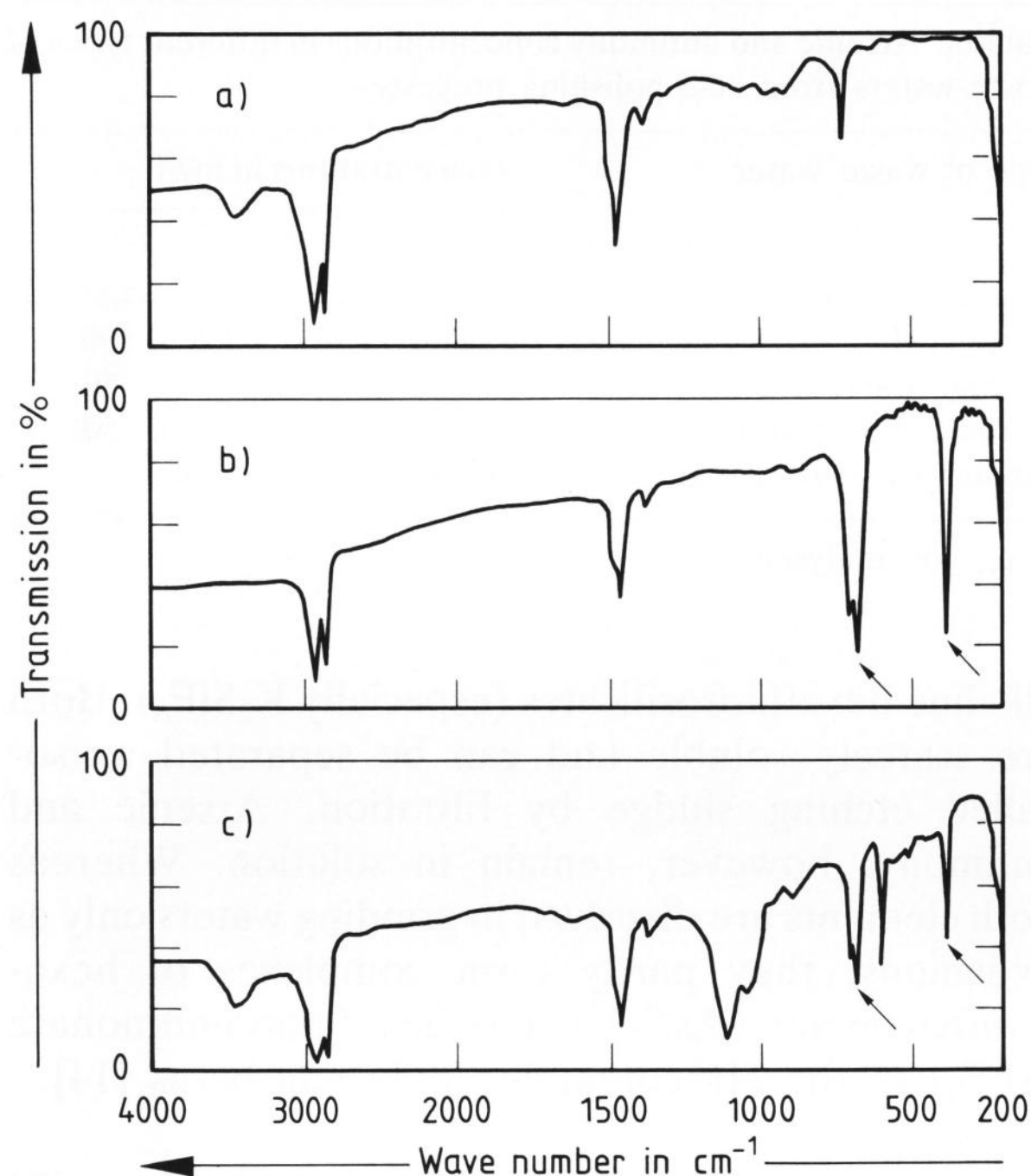
Contrary to oxygen anions of arsenic and antimony  $\text{AsF}_6^-$  and  $\text{SbF}_6^-$  complexes cannot be precipitated by iron ions. Therefore, the arsenic and antimony concentrations in polishing and washing

<sup>4</sup>) Since  $\text{AsF}_6^-$  cannot be reduced to  $\text{AsH}_3$  by  $\text{HCl}$  and zinc powder, all analytical methods based on this reaction consequently yield wrong data. The problem does not arise with ICP-OES (Inductive Coupled Plasma – Optical Emission Spectroscopy). Therefore, in this paper all concentrations of arsenic and antimony were determined by this method.

Table 2. Initial and residual concentrations of arsenic and antimony in different types of waste waters after precipitation with Fe<sup>3+</sup> ions

type of waste water	initial concentrations in mg/l		residual concentrations in mg/l	
	As	Sb	As	Sb
washing water	72.2	1.0	45.6	≤ 0.1
	17.9	2.6	14.8	1.1
	14.9	2.9	11.4	1.0
neutralization water	9.5	0.2	9.1	≤ 0.1
	4.9	0.9	3.9	≤ 0.1
exhaust gas rinsing water	12.9	n. f.	0.1	n. f.
	70.0	n. f.	0.2	n. f.

n. f.: not found.



Figures 3a to c. Infrared spectra of a) Noranium M2 SH 100, b) a solid precipitated by Noranium from a synthetic solution of KAsF<sub>6</sub> in water, c) a solid precipitated by Noranium from an acid polishing waste water.

baths as well as in neutralized waste waters remain quite high after iron precipitation. In waters from exhaust gas purification iron precipitation leads to acceptably low residual arsenic concentrations (table 2).

Experiments to remove the AsF<sub>6</sub><sup>-</sup> complexes by other state-of-the-art waste-water treatments, e.g. reduction reactions and sulphide precipitation, failed. Therefore, new reagents were searched for, which are able to precipitate AsF<sub>6</sub><sup>-</sup> and SbF<sub>6</sub><sup>-</sup> complexes, do not lead to further environmental problems, and which are not too expensive.

Laboratory experiments showed that large univalent cations (e.g. N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub><sup>+</sup>, P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>+</sup>) precipitate the hexafluoroanions in the different waste waters. In technical scale quaternary ammonium salts can be used. They are produced for applications as tensides mainly and do not harm the environment because they can be degraded biologically. The best results were obtained by "Noranium M2 SH 100" ((C<sub>n</sub>H<sub>2n+1</sub>)<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>Cl, with 12 ≤ n ≤ 18), a product of Ceca GmbH, Düsseldorf (FRG).

Figures 3a to c show the infrared (IR) spectra of the solid Noranium (figure 3a) and of the precipitated solid obtained by Noranium from a synthetic solution of KAsF<sub>6</sub> in water (figure 3b). The two bands at 395 and 690 cm<sup>-1</sup> corresponding to the two IR-active vibrations of the octahedral AsF<sub>6</sub><sup>-</sup> ion [15] can clearly be seen. They are also found in the spectrum of a precipitated solid obtained by Noranium from an acid polishing waste water (figure 3c). Absorptions at 615 and about 1100 cm<sup>-1</sup> indicate coprecipitated SO<sub>4</sub><sup>2-</sup> ions.

This precipitation with Noranium takes place even at lowest pH values (pH ≤ 0), so it is possible to separate the main content of arsenic (and antimony) in a small amount of solid waste before the water is neutralized, providing a low arsenic and antimony content in the neutralization sludge. Using this technique, the neutralization sludge probably has not to be disposed as hazardous waste. The oxoanions of arsenic and antimony in the neutralized water can be

Table 3. Initial and residual concentrations of arsenic and antimony in different washing waters from acid-polishing plants after different subsequent treatments

sample no.	initial concentration in mg/l		residual concentration in mg/l after					
	As	Sb	1st precipitation with Noranium		neutralization with Ca(OH) <sub>2</sub>		2nd precipitation with Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	
	As	Sb	As	Sb	As	Sb	As	Sb
1	8.6	6.7	2.8	n. c.	n. a.	n. a.	n. a.	n. a.
2	0.5	7.9	0.2	5.9	n. a.	n. a.	n. a.	n. a.
3	0.4	7.2	0.2	5.1	n. a.	n. a.	n. a.	n. a.
4	8.5	14.5	1.2	n. c.	≤ 0.1	10.2	≤ 0.1	0.4
5	10.9	16.1	3.5	n. c.	0.3	7.2	≤ 0.1	0.5
6	15.8	23.1	5.6	n. c.	0.7	8.7	0.2	0.7
7	12.4	30.3	3.0	n. c.	0.4	13.7	0.4	0.6

n. c.: not changed with respect to initial concentration. n. a.: not analysed.

removed by precipitation with iron ions in a second step.

In table 3 some results of this waste-water treatment carried out in laboratory-scale experiments are presented. For the precipitation of the  $\text{AsF}_6^-$  and  $\text{SbF}_6^-$  complexes a twofold molar excess of Noranium related to the whole arsenic and antimony content was used. After neutralization with  $\text{Ca}(\text{OH})_2$  to  $\text{pH} = 7$  to 8 the waste waters were treated with  $\text{Fe}_2(\text{SO}_4)_3$  to remove the remaining oxygen compounds of arsenic and antimony. This second step is analogous to the treatment of grinding waters. The results in table 3 show that antimony in contrast to arsenic is preferably removed by the second precipitation step. This can be explained by the fact that  $\text{SbF}_6^-$  partly hydrolyses and then can be precipitated by  $\text{Fe}^{3+}$  ions, whereas  $\text{AsF}_6^-$  is very stable [16] and therefore can only be removed by the Noranium precipitation step. The amounts of the two precipitation sludges are rather small ( $\approx 5$  wt%) compared with the neutralization sludge and have to be disposed as hazardous waste.

Figure 4 explains how this treatment can supplement existing equipments. Since all glassworks with acid-polishing equipments have a neutralization plant, only the two precipitation stations have to be installed additionally. The cleaned neutralization water can partly be recycled and, if necessary, can be used for washing remaining hazardous wastes out of the neutralization sludge so that it can probably be disposed into municipal landfills.

## 5. Summary

During the production of lead crystal and crystal glasses more than 95 wt% of the arsenic and antimony input remain in the saleable glasses and thus do not affect the environment. About 4.5 wt% of the arsenic and antimony input, set free by grinding and polishing processes, however, leaves the glassworks via sludges and waste waters. In grinding waters only oxoanions of arsenic and antimony are found. They can be removed by precipitation with  $\text{Fe}^{3+}$  ions. In waste waters of the acid-polishing process there are also  $\text{AsF}_6^-$  and  $\text{SbF}_6^-$  complexes which can be precipitated by the addition of quaternary ammonium ions. A two-stage waste-water treatment is described by which the oxo- as well as the fluoroanions of arsenic and antimony are removed from the waste waters, producing only a small amount of sludge which has to be disposed as hazardous waste. The corresponding neutralization sludge remains almost free of arsenic and antimony and can probably be disposed in municipal landfills.

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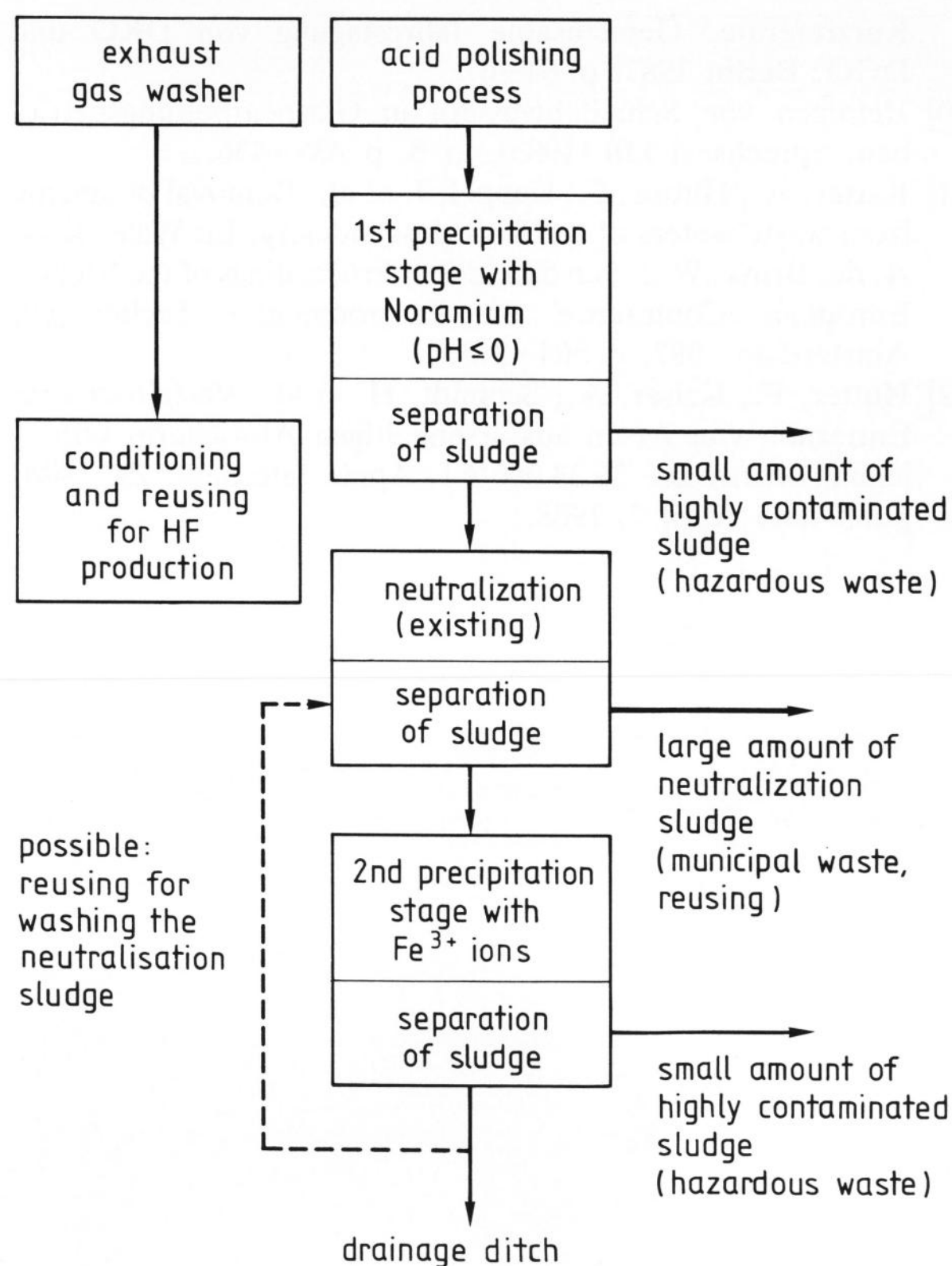


Figure 4. Flow chart for the treatment of waste waters from acid-polishing plants.

performing pilot- and production-scale tests and for financial support. They also thank the Umweltbundesamt, Berlin (FRG), the Bayerisches Staatsministerium des Inneren, München (FRG), and the Berufsgenossenschaft der keramischen und Glas-Industrie, Würzburg (FRG), for financial support. The experimental assistance of Ms. G. Müller and Mr. D. Schirdewahn is also gratefully acknowledged.

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