

REMOVAL OF ARSENIC FROM WASTE WATERS OF THE LEAD GLASS INDUSTRY

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1. INTRODUCTION

Arsenic trioxide (As_2O_3) is widely used as refining agent for the production of lead glasses /1/. Because of its toxicity there were attempts to reduce its consumption, which have been successful mainly due to an increasing number of electric melters. The As_2O_3 consumption within the glass industry of the Federal Republic of Germany decreased from about 300 t/a in 1981 to 145 t/a in 1985 /2/. But it was also shown that a complete renunciation of As_2O_3 is not possible up to now /3/. The possible substitution of As_2O_3 by Sb_2O_3 is not recommendable for toxicological and environmental as well as for economical reasons.

The As_2O_3 which is incorporated into the glass matrix during the melting procedure can be leached or dissolved, mainly during finishing procedures like grinding or acid polishing. Therefore, remarkable contents of arsenic in waste waters of lead glass plants are observed; Waste water originating from glass grinding process typically obtains 2 to 4 mg/l As, acid waste waters from chemical polishing even up to some 100 mg/l. In the Federal Republic of Germany no regulations concerning the arsenic content of waste waters of the glass industry exist due to the lack of avoidance. There are efforts, however, to set the limits for the arsenic concentration in waste waters significantly below 1 mg/l. For that reason, it is necessary to remove the arsenic from the waste waters before being drawn off.

Another serious problem arises from attempts to reduce water pollution by recycling the cooling water within the grinding process. The recycling basically offers two major advantages:

- the amount of waste water which has to be drawn off is reduced to about 5 % of the original amount,
- the temperature of the water can be kept at a higher level in order to decrease diseases at the glass grinder's arms.

State-of-the-art equipments for the recycling of glass grinding cooling water remove lead ions from that water satisfactorily /4/, but the arsenic content is not affected by that treatment. Therefore, arsenic concentrations in such circulating waters will increase significantly; values up to 10 mg As/l have been measured. A remarkable amount of the cooling water is sprayed as fine aerosols within the working area by high speed rotating grinding wheels. This can lead to health hazards due to their As_2O_3 content.

2. AIM OF THE WORK

Therefore, a technique should be developed with mainly two applications to be investigated: The As_2O_3 removal from recycled water of the grinding process and (within a series of preliminary experiments) the removal of As_2O_3 from other waste waters produced by lead glass plants. The new technology should be applied in a first step in combination with an installed lead precipitation unit, without disturbing its operation. The costs should be bearable to the plants and no secondary environmental problems should arise. The most promising techniques were planned to be evaluated first on laboratory scale. Then, in a pilot scale these techniques should be tested in order to find out the best parameters for the transfer into technical application.

3. STATE-OF-THE-ART METHODS IN REMOVAL OF ARSENIC FROM WASTE WATERS

Almost all papers dealing with the removal of arsenic from aqueous solutions are based on laboratory and a few pilot scale experiments. Mainly two general methods are described:

- adsorption techniques and
- precipitation reactions.

Adsorbents which have been tested for removal of arsenic, e.g. from ground or surface waters are activated charcoal, alumina, clays and materials based on titania /5 - 9/. Additionally, a method is described based on the reduction of the As(III) or As(V) to the oxidation state zero and the simultaneous adsorption at iron or zinc surfaces /10/. Thereby, arsenic contents could be reduced from some 10 mg/l to some 0.01 mg/l. Though it was not sure, that these techniques would work also with glass grinding waste waters, and though it was known that adsorption techniques would be relatively expensive, it was decided to take them into consideration at least within the laboratory scale experiments.

Most publications concerning the removal of arsenic from waste waters deal with precipitation reactions. The following precipitates are reported: arsenic sulphide, calcium arsenate and manganese arsenate /11 - 14/. Earlier publications reported in /15/ describe the precipitations of lead arsenate and magnesium ammonium arsenate. A third group of precipitation reactions is based on the addition of ferric salts to the arsenic containing solutions /16 - 19/.

Most of these reactions are described to be run in a pH range of about 6 to 11. Although it is well known that generally the solubility of As(V) compounds is less than that of As(III) compounds /15/, there is no distinction between As(III) and As(V). Starting from different concentrations of As, residual concentrations of 0.5 μ g/l to 0.7 mg/l are reported. Therefore, and due to the expected lower costs of precipitation techniques compared to adsorption, these possibilities should be investigated more in detail with respect to their application to glass grinding waste waters.

Only two papers present data from production scale arsenic removal techniques. The first report /11/ deals with the precipitation of As, but also Zn, Cu, Pb, Cd and Hg with sodium

sulphide from smelter waste waters. Since this process is optimized for the usual waste water composition of the smelter, a simple transfer to glass plant waste waters cannot be expected. The second method is the so-called "Skorodit-precipitation". It is used in a copper plant and works with ferric salts at pH = 1.9 to 2.0 if chloride ions are in solution or at pH = 2.7 to 2.8 if there are sulphate ions /20/. Grinding waters of the glass industry, however, show a pH in the range of 6 to 8.

In summary no commercially available process could be found from literature study to be easily adapted to the grinding process of lead glass production. Adsorption techniques and mainly precipitation reactions seemed to be promising enough to start laboratory scale experiments. For these experiments genuine waste waters of the lead glass industry were used in order to have all practical parameters included.

4. EXPERIMENTAL RESULTS

4.1. Laboratory scale experiments

The first experiments were done as batch experiments with recycled or non-recycled process waters. The samples contained between 2 and 4 mg/l As and 0.5 to 4.6 mg/l Pb. All analytical data for arsenic were obtained by ICP-AES (inductive coupled plasma - atom emission spectroscopy), which is specific for the element regardless of its oxidation state.

To reduce the arsenic content by adsorption TiO₂-modified silica gels, activated charcoal and alumina were used. Even in the best case only 15 % of the initial amount of arsenic were removed by these methods. No better results could be obtained by a combined reduction/absorption process on the surfaces of iron and zinc metals (table 1). Adsorbent to solution volume ratio and absorption periods were varied in order to make sure that the important range of the adsorption isotherms were covered.

As also can be seen from table 1, most of the precipitation experiments did not yield in a sufficient removal of arsenic within these batch experiments. Addition of sulphide, ammonium, magnesium, manganese, lead or aluminium ions did not reduce the arsenic content remarkably. Variations of concentration of precipitating agent, pH, reaction times, temperatures as well as addition of H₂O₂, hypochlorite or KMnO₄ in order to oxidize the As(III) to As(V) did not increase the effect. Therefore these variations are not indicated in table 1.

Favourable results, however, were obtained with iron(III) ions, coprecipitating arsenic with iron hydroxide (presumably as FeAsO₄ /20/. The arsenic concentration could be reduced to less than 0.5 mg/l when 50 mg/l iron(III) ions were added (as aqueous solutions of FeCl₃, Fe₂(SO₄)₃, FeClSO₄ or NH₄Fe(SO₄)₂) to the batches. The type of Fe(III) salt added did not influence the result. The influence of the amount of Fe(III) ions added to the waste water is shown in figure 1, which also demonstrates that without addition of oxidizing agents much higher amounts of Fe(III) ions are necessary to obtain similar results. The values of As concentration indicated in figure 1 are obtained only when the residence time (time

between addition of iron ions and filtration) is kept above 12 minutes. Therefore, in a continuous process a buffer tank which allows a sufficient residence time has to be provided.

TABLE 1. Representative data of laboratory scale batch experiments to remove arsenic from glass grinding waste waters (Initial amount of arsenic: 4.0 mg/l).

Method	% of arsenic removed	Residual amount of arsenic (mg/l)
Adsorption on:		
- SiO ₂ /TiO ₂	< 3	> 3.8
- Activated charcoal	< 3	> 3.8
- Alumina	15	3.4
- Metal surface of:		
- Fe	< 2	> 3.9
- Zn	17	3.3
Precipitation as:		
- As ₂ S ₃ , As ₂ S ₅	20	3.2
- NH ₄ MgAsO ₄	< 1	> 3.9
- Mn ₃ (AsO ₄) ₂	< 1	> 3.9
- Pb ₃ (AsO ₄) ₂	< 1	> 3.9
- AlAsO ₄	20	3.2
- FeAsO ₄	> 85	≈ 0.5

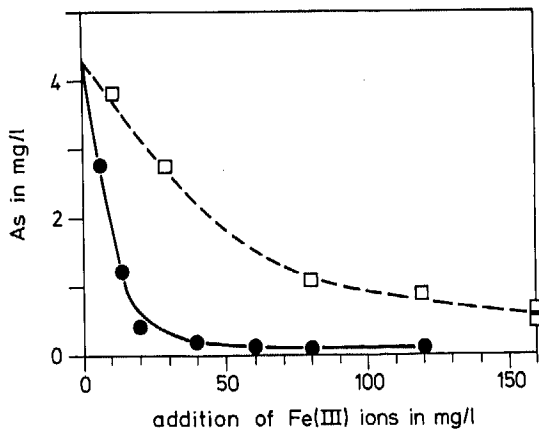


FIGURE 1. Remaining concentration of arsenic after precipitation with Fe(III) ions

- : sample oxidized by H₂O₂, hypochlorite or KMnO₄
- : untreated sample.

Since in industrial lead removal procedures CO_2 is injected to precipitate lead ions as PbCO_3 , analogous experiments were carried out to find out whether the As precipitation process affects that reaction. No inhibition effect could be seen. All solids suspended in the grinding water (glass particles, PbCO_3 , FeAsO_4 , Fe(OH)_3 , flocculants) could be filtered off together without any difficulties.

Based on these results, it was decided not to investigate the adsorption techniques any longer, and continuous pilot scale experiments with precipitation of arsenic by Fe(III) ions were planned.

4.2. Pilot scale experiments

A pilot scale equipment was designed in which the water supply for ten glass grinder operating positions was recycled with precipitation of lead as PbCO_3 , flocculation and filtration. The average flow rate was about 400 l/h. Into a buffer container installed upstream the location where CO_2 was added to form lead carbonate, a solution of FeClSO_4 and oxidation and neutralization agents were added. With this equipment the influence of different parameters (listed in table 2) was investigated. Figure 2 shows the concentrations of arsenic and lead in the water circuit during periods under different conditions. In periods indicated by "X" no addition of Fe(III) took place. Chloride content (resulting from FeClSO_4 addition) was monitored in order to see to which extent its concentration increases.

TABLE 2. Addition of oxidizing and neutralizing agents in the pilot scale experiments (see figure 2). Amount of Fe(III) ions: 0.87 mmol/l of circulating water.

Period	Addition of H_2O_2 (mmol/l)	Addition of neutralizing agent (mmol/l)
A	2.52	3.62 NaHCO_3
B	No addition	3.62 NaHCO_3
C	2.52	1.35 Ca(OH)_2
D	No addition	1.35 Ca(OH)_2

As indicated in figure 2 (and proved within the experiments reported in chapter 4.3), oxidation with H_2O_2 was not necessary. The reason for that surprising effect is not yet clear. Perhaps, there is an oxidizing effect when the water gets into contact with oxygen of the air during the recycling. Bubbling oxygen through the batch samples within the laboratory scale experiments did not lead to a similar effect, however. This difference can be due to the fact that the waste waters used in the laboratory scale experiments have aged because of the shipping procedure.

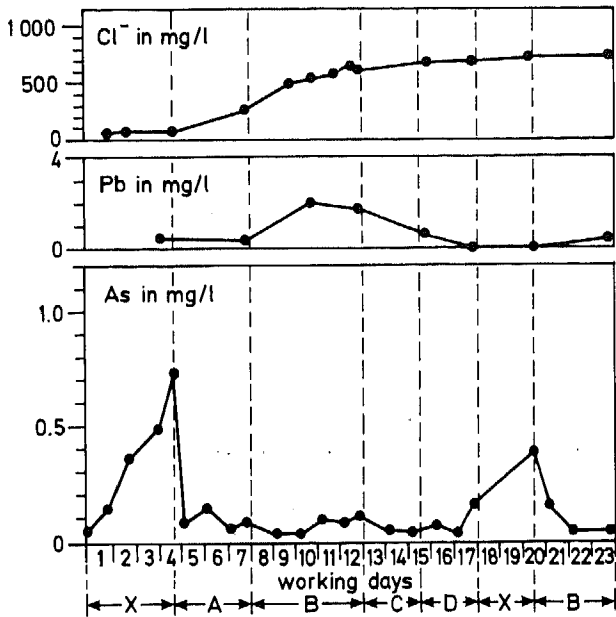
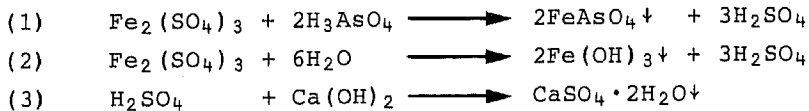


FIGURE 2. Concentrations of arsenic, lead and chloride within the water circuit during the pilot scale experiments. Explanations to periods A to D see table 2; in periods indicated by "X" no Fe(III) was added

Like in the laboratory scale batch experiments, an arsenic concentration of 0.1 mg/l or less could be maintained within these pilot scale tests. Neutralization by a NaHCO_3 solution is possible, but using Ca(OH)_2 suspension is cheaper and can keep the sulphate concentration at about 1 g/l. This is especially advantageous when $\text{Fe}_2(\text{SO}_4)_3$ is used instead of FeClSO_4 in order to avoid secondary problems by increasing chloride ion concentration. In this case the overall reactions formally can be described by equations (1) - (3):



The PbCO_3 precipitation again was not affected by the arsenic removal. Concentrations of far less than 1 mg/l lead ions were maintained. The higher lead concentrations during experiment B were caused by insufficient CO_2 supply. As in the laboratory experiments, all solids suspended in the circulating water could be filtered off without any problems.

4.3. Production scale experiments

Based on the encouraging results of the pilot scale tests an additional experiment with the grinding water of a whole lead crystal glass plant was performed. A flow chart of this system is given in figure 3.

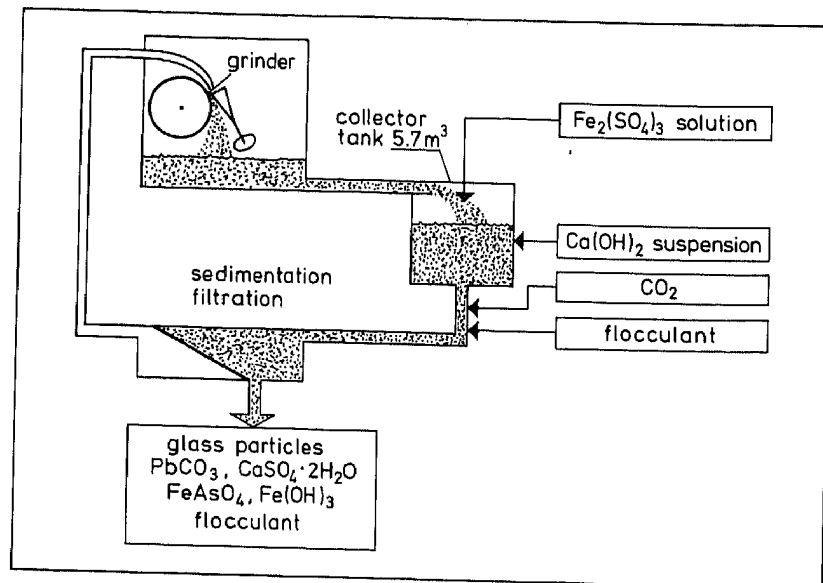


FIGURE 3. Flow chart of the equipment for the production scale experiment.

The flow rate during day shifts was about 16 m³/h, during night shifts, lower and changing flow rates occurred. Therefore addition of iron(III) ions was not possible and the arsenic concentration increased during night time. Iron(III) ions were added as an aqueous solution of Fe₂(SO₄)₃, which was neutralized by the stoichiometric amount of a Ca(OH)₂ suspension. Figure 4 shows the content of arsenic and lead in the water circuit during this experiment. When iron(III) ions were added, the arsenic concentration decreased to a level of about 0.1 to 0.2 mg/l. The efficiency of arsenic removal could be influenced by the amount of Fe(III) ions added which was varied within the periods A to D (see figure 4). The velocity of lowering the arsenic content of the circulating water depends on its initial concentration. It can be assumed that continuous addition of iron ions controlled by the actual flow rate can stabilize an arsenic level as low as 0.1 mg/l.

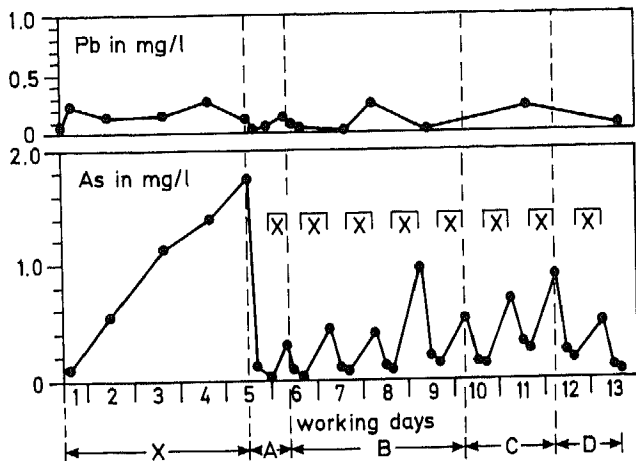


FIGURE 4. Concentration of arsenic and lead during the full scale experiment. Addition of iron ions in mmoles/l within the different periods: A 0.90, B 0.30, C 0.15, D 0.25. In periods indicated by "X" no iron ions were added.

Again, the removal of lead was not affected. Lead ion concentrations could be kept well below 0.5 mg/l. The iron arsenate and hydroxide precipitates sedimented well and could be filtered, as long as not more than about 1 mmole/g iron ions had been added and a reaction time of at least 20 minutes could be provided.

After this period which is documented in figure 4 the whole equipment was operated in the same way another three months without problems. After that, some difficulties arose which are mainly due to the lack of controlling and regulating. Therefore in the next step an equipment has to be provided with dosing unit controlled by the flow rate for the iron and $\text{Ca}(\text{OH})_2$ addition.

The solid waste filtered off during operation of the arsenic elimination, showed a slightly increased leachability of arsenic compared to the usual grinding sludge. The increase in leachability, however, was not as high as to produce a new quality of waste.

4.4. Removal of arsenic in other waste waters

In a series of additional experiments it was tried to use these excellent results of arsenic removal from glass grinding waste waters also for other arsenic containing waters in glass plants, e.g. from acid polishing process or from the neutralization unit. These experiments failed up to now, however. The reason for that is not yet known, but maybe fluoride containing arsenic compounds produced in the polishing process play an important role. Further research and development activities to overcome these problems are under work.

5. SUMMARY

A new technology was developed to remove arsenic from waste waters of the lead glass grinding process. The method is based on the well known precipitation of arsenic with iron(III) ions. It allows the residual amount of arsenic to be kept at or even below 0.1 mg/l, also when used in combination with state-of-the-art lead removal techniques. The additional costs are low compared to those of the usual water recycling process with lead removal technologies. The process does not create any secondary environmental problems.

6. REFERENCES

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