Refining of lead glass using As(III)/Sb(III) or As(V)/Sb(V)

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Det här är en undersökning som knyter an till en tidigare publicerad artikel om nitratfri luttring av ett soda-kalk-glas[1]. Det är ur miljösynpunkt bättre att använda antimonat som luttringsmedel efter som utsläppen av NO_x-gaser blir betydligt mindre då inget nitrat tillsätts. Antimonat ger i soda-kalk-glaset lika god luttrande effekt som nitrat och antimonoxid. I den här artikeln har studien utökats med en undersökning av ett blyglas. Luttringsegenskaperna för en blandning av arsenik och antimonoxid jämförs med motsvarande arsenat och antimonat och det visade sig att arsenat inte är så effektivt som luttringsmedel medan antimonat har i princip samma effektivitet som antimonoxid.

Introduction

The refining of crystal/handmade glass is often achieved by using a redox-reaction where arsenic and/or antimony oxide are oxidised by nitrate. The trivalent metal is oxidised to the pentavalent state. The equilibrium between the two different oxidation states can be described according to the following equation.

$$M_2O_3+O_2 \leftrightarrow M_2O_5$$

where M= As or Sb

At higher temperatures the reaction is shifted to the right and oxygen will be released into the melt. The efficiency of arsenic and antimony has been compared in earlier studies. Cable *et al.* compared their results of antimony refining of a soda-lime-silica glass with earlier results of arsenic refining and their results suggest that antimony is a more efficient refining agent than arsenic [2]. The study is based on counting seeds, size distribution of seeds and the gas content of the seeds. An electrochemical study by Claußen *et al.* describes the refining by the temperature of maximum fining, T_p, and the highest amount of oxygen formed as a function of temperature, ΔO_2(max). Their results give a higher value of ΔO_2(max) and a lower value of T_p for antimony than for arsenic in a soda-lime-silica glass and a borosilicate glass [3]. Hupa *et al.* melted soda-lime-silica glass at a temperature of 1350 °C and when comparing arsenic to antimony they found by counting bubbles that antimony was a more efficient refining agent than arsenic at this temperature [4]. Schönborn also did comparative studies between refining with arsenic and antimony in a soda-lime-silica glass and found antimony to be more efficient than arsenic [5]. For a soda-lime-silica glass antimony seems to be a better choice than arsenic. Another advantage is that antimony is less toxic than arsenic.

The addition of nitrate increases the emission of NO_x from the batch.

The nitrate is used to oxidise the trivalent antimony to the pentavalent state. So if Sb(V) was added to the batch it would not be necessary to add nitrate. Springer reported test results for use of antimonate as a refining agent already in 1940. His results indicated that it would be a better refining agent in lead glass than in lead free glasses [6]. For television glass production a combination of antimonate and nitrate are used [7]. This addition of nitrate ought to be unnecessary. A study by Jonson investigated the possibility of refining without using nitrates [1]. He successfully refined an unleaded glass using antimonate. The aim of this study is to see if it is possible to successfully refine a lead glass with antimonate as well. The refining effect will always depend on the composition of the base glass. To make a relevant comparison the refining was done both with mixtures of trivalent and with mixtures with pentavalent arsenic and antimony as refining agents.

Experimental

The base glass corresponding to a 24% PbO crystal glass, is specified in table 1 was used. The total molar amount of arsenic and antimony were kept constant but the proportions between antimony and arsenic were varied. Refining was done both with nitrate and arsenic and/or antimony oxide as well as only arsenate, Na_2HAsO_4, and/or antimonate, $NaSbO_3$. The amounts of nitrate were varied, mostly $NaNO_3$ was used but KNO_3 was also tested. The additions of $NaNO_3$ were 3, 6 and 9 kg and for KNO_3 11 kg per 100 kg sand. All the chemicals except arsenate were of industrial grade.

The glass batch corresponding to 268 g glass was added in two charges into a ceramic crucible and melted at 1420 °C. The second charge was added 8 min after the first. The melted glass was formed in a ring shaped form with a diameter of 78 mm. The glass was moved across a carbon block until solid, which gave an even bottom. The pieces were annealed carefully. The bubbles were counted in just the central 60 mm of the sample by covering the edge. An imaging processing system using a video camera and the Sky Instrument Ltd V1.1a imaging software was used for analysing. Due to computer performance some of the pieces with a lot of bubbles had to be measured in half or quarter size. When the number of bubbles are very high the accuracy decreases as bubbles will be overlapping and thus are counted as one or none if the total area becomes greater than what will be counted. The number of bubbles are given as bubbles per 100 g glass. At least two samples of each combination were made. There is a slight variation in which area of the piece that is measured and the bubble distribution is not perfectly homogeneous. Especially with fewer bubbles the number of bubbles measured will depend on which area of the piece is used. The same piece with ca 350 bubbles was measured repeatedly and the maximum variation of bubbles was 45. The variation could thus be estimated to around 10 %. Bubble size estimations showed no change with varied refining agent.

Table 1 *The composition of the used base glass in mole% for the different fractions antimony of total amount arsenic and antimony.*

Oxide	0 Sb	0,25 Sb	0,35 Sb	0,75 Sb	1,00 Sb
SiO_2	73,80	73,80	73,80	73,80	73,80
Na_2O	3,75	3,75	3,75	3,75	3,75
K_2O	11,34	11,34	11,34	11,34	11,34
PbO	8,94	8,94	8,94	8,94	8,94
ZnO	0,96	0,96	0,96	0,96	0,96
Al_2O_3	0,03	0,03	0,03	0,03	0,03
B_2O_3	0,88	0,88	0,88	0,88	0,88
As_2O_3	0,31	0,23	0,20	0,08	
Sb_2O_3		0,08	0,11	0,023	0,31

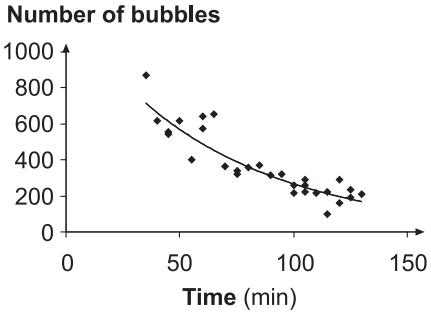

Figure 1 *The number of bubbles as a function of the total melting time.*

Refining time. Different refining times were tried for the glass with 0,35 Sb using oxides and nitrate as refining agents (fig. 1). There is a certain amount of variation for each refining time but the number of seeds as a function of time approximately follows an exponential relationship in agreement with the observations of Cable [8]. A refining time of 100 minutes gives around 300 bubbles and that is a low enough number to be quite accurately counted. This refining time was used for all following experiments.

Results and discussion

Refining with nitrate and trivalent oxides

The results of refining with Sb(III)/As(III) are given in figure 2-4 and table 2. Although there is quite some variation in the results of the individual pieces with the same compo-

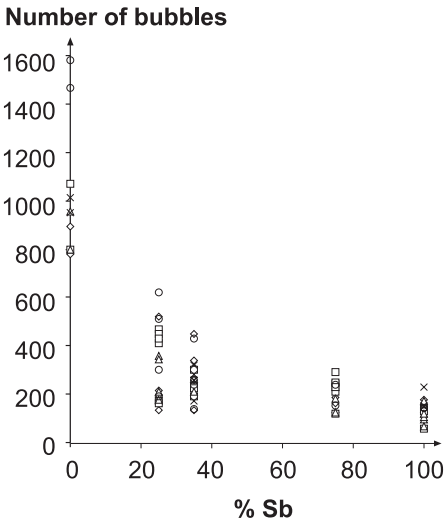

Figure 2 *Number of bubbles as a function of the antimony content, see table 1. The Sb(III)/As(III) series are represented with diamonds (◇) when 3 kg of $NaNO_3$ are added, with squares (□) for 6 kg $NaNO_3$, with triangles (△) for 9 kg $NaNO_3$, while the cross (×) is with addition of 11 kg KNO_3 and the circles (●) are for the Sb(V)/As(V) system. All amounts are additions per 100 kg sand.*

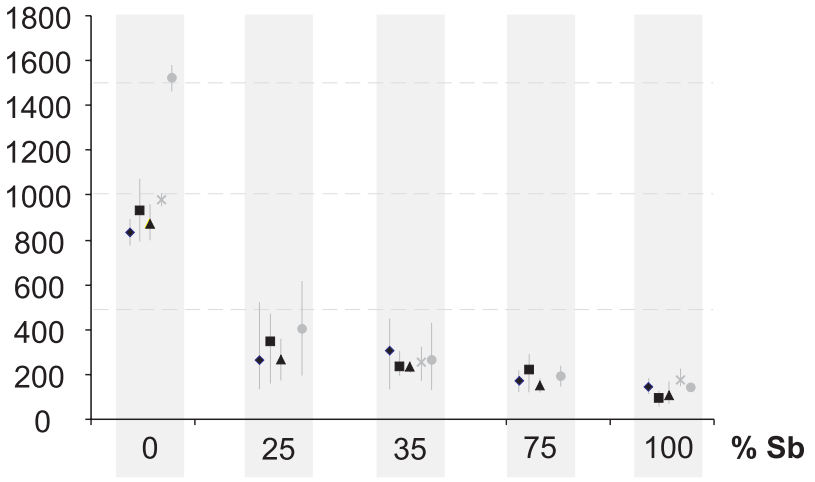

Figure 3 *Simplification of figure 2. The mean value of the number of bubbles found is plotted for the different fractions of added Sb and the error bars shows the variation in the number of bubbles. The addition are represented by ♦ for 3 kg $NaNO_3$, ■ for 6 kg $NaNO_3$, ▲ for 9 kg $NaNO_3$, × for 11 kg KNO_3 for refining with Sb(III)/As(III) and ● for refining with Sb(V)/As(V).*

Table 2 *The results of the bubble measurements. Nr is the number of repeated samples. The maximum, minimum and mean number of bubbles, respectively are given.*

Description	Fraction Sb	Nr	Bubbles		
Sb(III)/As(III)			*Max*	*Min*	*Mean*
3 Kg $NaNO_3$	0,00	2	891	779	835
	0,25	4	521	132	266
	0,35	4	450	135	308
	0,75	4	217	124	171
	1,00	4	177	107	140
6 Kg $NaNO_3$	0,00	2	1071	798	935
	0,25	6	468	163	348
	0,35	3	303	190	239
	0,75	6	291	119	223
	1,00	2	130	58	94
9 Kg $NaNO_3$	0,00	2	955	797	876
	0,25	4	360	179	272
	0,35	2	260	209	235
	0,75	2	183	123	153
	1,00	5	170	69	111
11 Kg KNO_3	0,00	2	1011	950	980
	0,35	4	322	174	258
	1,00	3	227	146	175
Sb(V)/As(V)	0,00	2	1583	1466	1524
	0,25	4	620	191	406
	0,35	4	428	137	266
	0,75	2	237	151	194
	1,00	2	145	144	144

sition there is no doubt that antimony is a more efficient refining agent than arsenic in this base glass. There is almost 10 times as many bubbles detected in the glass refined with arsenic compared to antimony. The better refinement with antimony is also very clear by visual judgement as seen from figure 3. When the amount antimony is increased the number of bubbles decrease and the spread of the number of bubbles decreases also somewhat. Already when 25 % antimony is added, the number of bubbles decreases drastically. The superiority of antimony to arsenic in refining is in agreement with results from earlier studies [2-4]. One of the reasons why antimony is a better refining agent than arsenic is that a higher temperature is needed to oxidise arsenic. To oxidise 50 % of the antimony in a lead glass to the pentavalent state a temperature of 1200 °C is needed while for arsenic the corresponding temperature is 1400 °C [9]. More arsenic is also lost from the melt as it is more volatile than antimony.

The amount of the oxidiser was varied. There is no major difference between the different series but there is a tendency for less variation in the bubble count when the amount of oxidiser is increased, see

figure 3. This is most clear for the batches with 0,25 or 0,35 Sb, see also table 2. For refining with only antimony the mean number of bubbles is slightly higher for the lowest level of oxidiser, 140 bubbles compared to 94 and 111. This could be an indication that the lowest level might not be a large enough excess to oxidise most of the antimony(III) to antimony(V). Jonson observed a slight improvement in refining of a soda-lime-silica glass (composition in weight% 70 SiO_2, 10 Na_2O, 9 K_2O, 10 CaO and 1 B_2O_3) with increasing amount $NaNO_3$ for corresponding addition of Sb [1]. The results of this investigation might indicate a similar tendency.

Jonson found that for a base glass without lead there was no significant difference between the two oxidation agents KNO_3 and $NaNO_3$ [1]. As seen from figure 2 and 3, where crosses are used for the experiments with addition of KNO_3, this is probably also true for the lead crystal using arsenic or a combination of arsenic and antimony. The only combination where there is a difference is for refining with only antimony. The number of bubbles is a little higher for KNO_3 refining as the mean value is 175 bubbles, compared to 111 bubbles as found for similar amounts of $NaNO_3$, see table 2. Not even the lowest addition of $NaNO_3$ gives so many bubbles.

Refining with pentavalent oxides

The main difference between the tri- and the pentavalent state is that arsenate is definitively a worse refining agent than arsenic, see figure 2-3. The mean number of bubbles is 1500 for refining with pure arsenate compared to 1000 or less for arsenic oxide refining, see table 2. For antimony this difference is not observed. Pure antimonate refining gives around 140 bubbles while antimony(III) oxide gives somewhat fewer, around 100 bubbles. The

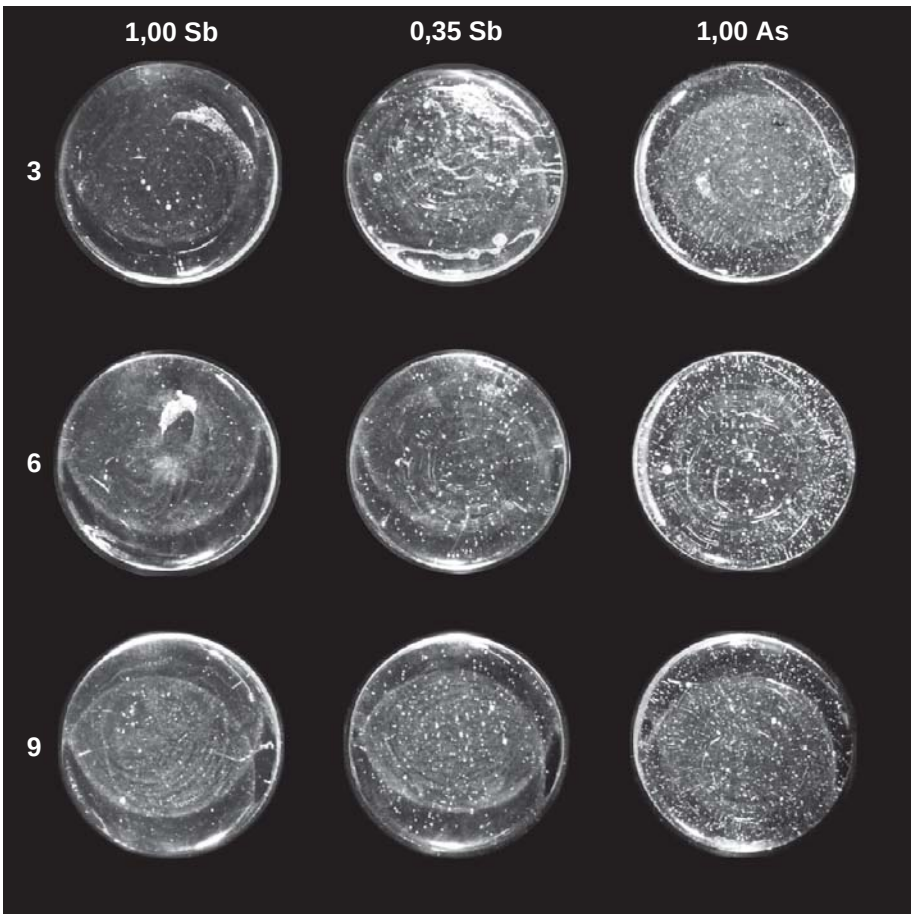

Figure 4 *The variation in bubbles for pieces with varying amount nitrate, 3, 6 or 9 kg added $NaNO_3$ per 100 kg sand, and different fractions of antimony, 1,00 Sb(III), 0,35 Sb(III) or 1,00 As(III). The bubbles show up as light spots.*

antimonate refining is equal to the results achieved with antimony(III) oxide and the lowest amount of added nitrate. The variation is as for the trivalent oxide refining, less when the amount of antimony is increased compared to the arsenic.

The experiments are based on an optimised recipe using 0,35 antimony(III) oxide and 0,65 arsenic(III) oxide. The number of moles of refining agent is kept constant and the proportions of the components are varied. When compared with arsenate and antimonate the same number of moles is used. This might not be the optimum number of moles for antimonate refining so the results could probably be improved somewhat by varying the addition of antimonate, compare with the improvement achieved by higher additions of nitrate for antimony(III) oxide refining.

Springers refers to factory experiments with antimonate where the refining of a lead free glass did not give good enough results while it worked fine in a lead containing glass [6]. Jonson found that antimonate seemed to be as efficient as antimony(III) oxide in the investigated soda-lime-silicate glass [1]. Our results show that antimonate gives similar results as antimony(III) oxide in a 24% PbO base glass. In these experiments there is no indication of antimonate being a better refining agent in a lead glass than in a regular soda-lime-silicate glass

as Springer suggested.

Conclusions

When comparing arsenic(III) oxide, antimony(III) oxide and mixes between the two, refining with antimony alone is most efficient in the studied lead glass. There is an almost 10 fold improvement with antimony(III) oxide as refining agent. The mixtures also give a good refinement but the variation between different samples is somewhat bigger. Arsenic is more toxic than antimony and as there is no improvement by arsenic additions antimony refinement is to be recommended.

Arsenate is not a very good refining agent while antimonate is as good as antimony(III) oxide. When the effects on the environment are taken into account as well antimonate should be preferred as no nitrate is added and the emission of NO_x is thus reduced drastically.

Acknowledgement

The author wants to thank Dr. Bo Jonson for his valuable input.

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