THE BEHAVIOUR OF PHOSPHORUS IMPURITIES IN ALUMINIUM ELECTROLYSIS CELLS

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Abstract

Phosphorus is an important impurity element in the Hall-Heroult process, where it affects the current efficiency with respect to aluminium and the metal quality. The chemical and electrochemical behaviour of phosphorus compounds in molten cryolite-base electrolytes was studied in controlled laboratory experiments. Measurements were also carried out in industrial cells by analysis of bath and metal as a function of the time after additions of phosphorus compounds to the electrolyte. Phosphorus has a relatively long residence time in the electrolyte compared with metallic impurities such as iron, silicon and titanium. Phosphorus escapes from industrial cells through evaporation of elemental phosphorus or as a phosphorus compound attached to small carbon particles (carbon dust). It was found that only small amounts of phosphorus are primarily deposited at the cathode. A relatively minor increase of the normal operating temperature was found to cause a drastic decrease of the amount of phosphorus in aluminium.

Introduction

Impurities present in the Hall-Heroult process originate mainly from the raw materials, carbon and alumina. Some additional impurities come from bath components (AlF_3), tools, anode stubs and sidelining (SiC) and refractory lining materials. The major part of these impurities is initially present in the electrolyte as dissolved fluoride or oxyfluoride complexes. The dissolution process can be expressed as follows:

$$3MO + 2AlF_3 = 3MF_2 + Al_2O_3 \qquad (1)$$

for a divalent cation. The concentration of impurities in the bath is normally well below saturation [1]. In most cases the decomposition voltage of MO is lower than that of Al_2O_3 so that M will be reduced at the cathode and end up in the produced aluminium. It has been shown by Johansen et al. [2] that the transfer of iron from the bath to the metal was mass transfer controlled. According to this mechanism an impurity element will be reduced at the cathode at its limiting current density (i_{lim}), which depends on the concentration of the element in the bath (c^o) and the mass transfer coefficient (k_m):

$$i_{lim} = nFk_mc^o \qquad (2)$$

The mass transfer coefficient increases with increasing convection.

Phosphorus is mainly introduced with the alumina, most likely in the form of an oxide (P_2O_5) or a phosphate ($AlPO_4$). Due to increased recycling of impurities with secondary alumina from modern dry scrubbers, more phosphorus ends up in the electrolyte and in the produced aluminium than in the past. Phosphorus and its compounds can appear in several different valence states, from –3 to +5. In industrial cells the phosphorus content shows large variations; from 10 ppm up to about 200 ppm in the electrolyte an from 1-5 ppm to about 20 ppm in the produced aluminium. Phosphorus is an unwanted impurity for several reasons. Even very low contents of phosphorus in aluminium will reduce the corrosion resistance and increase the brittleness of the metal.

Also important is the negative effect of phosphorus containing compounds in the electrolyte leading to a reduced current efficiency. This is due to cyclic oxidation and reduction reactions at the electrodes involving different valence states of phosphorus. In certain cases up to 50% of the loss in current efficiency due to impurities can be ascribed to phosphorus [3, 4].

Various studies in industrial plants have shown that most of the phosphorus entering the cells with the alumina primarily leaves the cell with the exit gas, suggesting that volatile phosphorus compounds are formed [5, 6]. However, laboratory studies have shown that the vapour pressure of the electrolyte does not increase significantly in the presence of dissolved phosphorus compounds [7]. A possible link between phosphorus in the bath and carbon dust may be important for explaining the behaviour of phosphorus. It has been suggested that phosphorus is adsorbed by small carbon particles in the bath, and thus the residence time for phosphorus in the bath increases, and eventually a large portion of the phosphorus is skimmed off the cells with carbon dust [6, 8]. This mechanism may be especially important for Søderberg cells. Very high contents of phosphorus have been analysed in samples of carbon and anode cover material from industrial cells [9]. Phosphorus may escape from the cells as gaseous elemental phosphorus gas formed at the cathode and with the particulate emissions [10]. A certain fraction of the phosphorus in the exit gas may escape through the dry scrubber.

Results and discussion

Electrochemistry

Laboratory experiments were carried out to study the electrochemical behaviour of dissolved phosphorus species in cryolite-alumina melts. Cyclic voltammetry showed that additions of $AlPO_4$ and Na_3PO_4 gave rise to several reduction and oxidation reactions within the stable potential range (electrochemical window) for dissolved alumina. Figure 1 shows cyclic voltammograms obtained at a tungsten electrode in molten cryolite saturated with alumina before and after addition of $AlPO_4$. The anodic potential is limited by the dissolution of tungsten at ~1 V vs an aluminium reference electrode. The presence of dissolved phosphorus species due to addition of $AlPO_4$ gave rise to a broad cathodic current response and a corresponding anodic current peak, the latter likely to be due to oxidation to a P(V) species. No clear reduction peak representing the formation of elemental phosphorus could be detected.
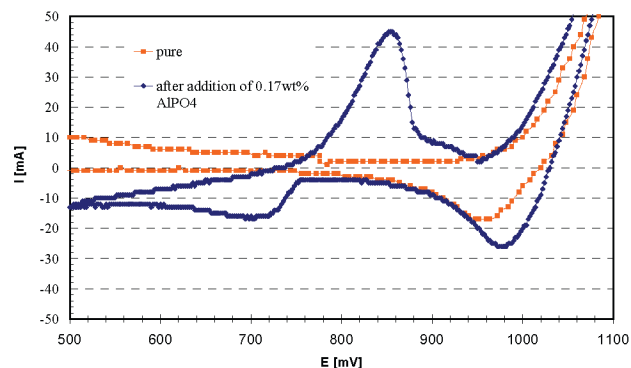

Figure 1: Cyclic voltammograms at a tungsten electrode in molten Na_3AlF_6-Al_2O_3(sat.) at 980°C before and after addition of $AlPO_4$ (0.17 wt%). Sweep rate: 200 mV/s.

Behaviour of phosphorus in industrial cells

Several measurements were carried out in industrial cells, where phosphate ($AlPO_4$ and Na_3PO_4) were added to the bath together with compounds of other impurity elements such as iron and silicon. Samples were taken from the bath and from the metal for analysis.

Bath samples were analysed by XRF. Metal samples were analysed with an automated emission spectroscope.

Figure 2 shows the concentrations of phosphorus and silicon in the electrolyte as a function of time before and after additions of $AlPO_4$, Na_3PO_4 and SiO_2. Treatment of the results shows that the decrease in the Si content in the bath with time corresponds well with mass transport controlled deposition of Si at the aluminium cathode; and most of the added silicon is primarily being reduced at the cathode. Similar results were obtained for iron and titanium. However, the decrease in the phosphorus content was much slower. A possible explanation is that gaseous phosphorus is formed at the cathode, most of which leaves the cathode and gets oxidised in the bath. This cycle may be repeated several times causing a longer residence time in the bath of phosphorus and hence an adverse effect on the current efficiency.
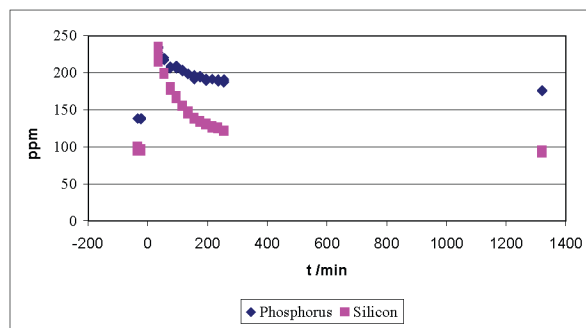

Figure 2: Concentration of phosphorus and silicon in the bath as a function of time after addition of silica and phosphate.

The phosphorus content in the metal remained fairly constant during the first four hours following an initial increase right after the additions were made, whereas the phosphorus content in the bath decreased by about 18% in the same period. This indicates that most of the added phosphorus initially remains in the electrolyte, and some escaping with the exit gas. Sampling at 22 hours after the additions were made showed a small increase of the phosphorus content in the metal.

Phosphorus and process variables

Data for the phosphorus concentration in aluminium produced from individual industrial cells were used to obtain correlations with several process variables. Analysis of electrolyte and metal for a large number of cells showed that the ratio of the average concentrations of phosphorus in the bath and in the metal was nearly constant. The ratio was found to be about 10 (ppm P_{bath}=10 ppm P_{Al}) even for large variations of the phosphorus content during short periods.

Temperature

The concentration of phosphorus in the metal varies from line to line. Figure 3 shows the phosphorus content in the metal for the prebake and Søderberg lines at the Hydro Aluminium plant in Årdal. The P concentration in the Søderberg line was close to the detection limit of the metal analysis, which is approximately 2-5 ppm. In the prebake line the average concentration was 8-15 ppm.
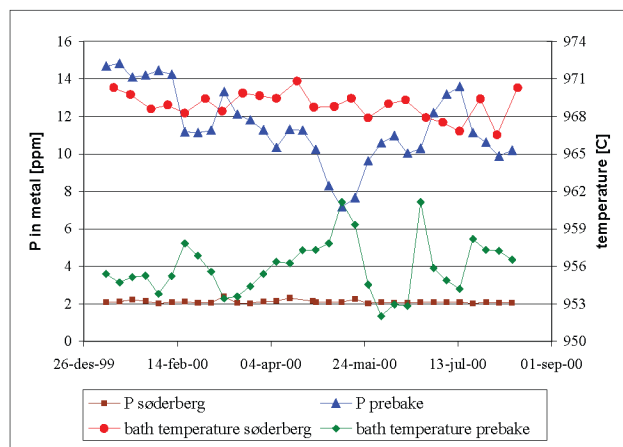

Figure 3: Average values for the phosphorus content in aluminium and the bath temperature for Søderberg and prebake cells at the Hydro Aluminium plant in Årdal.

The Søderberg line is fed with primary alumina, while the prebake line is fed with secondary alumina from the dry scrubber. Hence one should expect a lower phosphorus content in the Søderberg cells. Another obvious difference between the prebake and the Søderberg line is the average bath temperature. As can be seen from Figure 3 the average bath temperature is 965-970 °C and 950-960 °C in the Søderberg line and the prebake line

respectively. The phosphorus content in the metal seems to be inversely proportional to the temperature for the prebake line.

Other observations indicate that the phosphorus content in the metal is determined mostly by the temperature. Figure 4 shows average values for the phosphorus content in the metal and the bath temperature as a function of time for a large number of prebake cells. Considering the relatively small temperature variations there seems to be a clear correlation between high phosphorus in the metal and low temperature.

Variations in temperature are usually linked with variations in the electrolyte composition. In other cases changes of the interpolar distance and disturbances such as anode failures may be responsible for temperature variations. In the present study no attempt was made to relate the variation in phosphorus content to the possible effects of these variables.
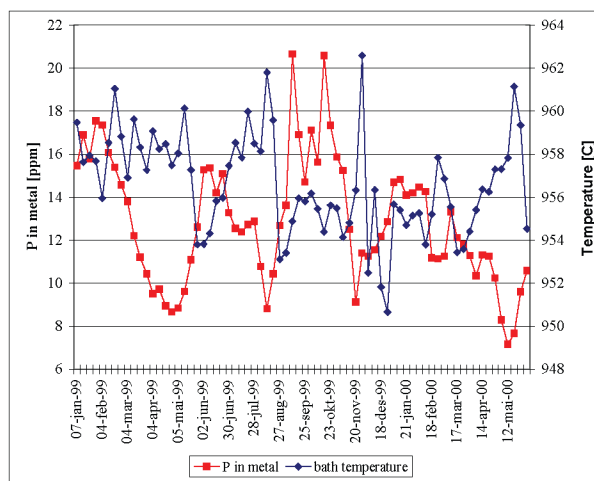

Figure 4: Average values for the phosphorus content in aluminium and bath temperature for prebake cells as a function of time.

Figure 5 shows the relationship between the phosphorus content in the bath and the temperature measured over a period of two months for one particular cell. The results show that variations in temperature are reflected by inverse changes in the phosphorus content in the bath.
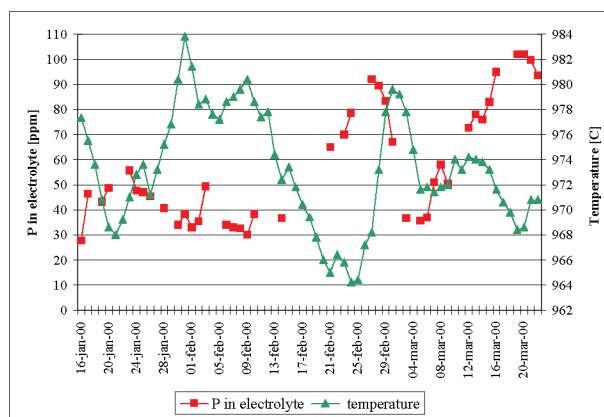
Figure 5: Phosphorus content in the bath and bath temperature for one prebake cell as a function of time.

Anode effect

Analysis of aluminium produced in periods before and after anode effects showed that the phosphorus content in aluminium decreased dramatically after the occurrence of an anode effect. As expected the temperature increased during the same periods. Other effects than the temperature increase, such as increased electrolyte convection and reduced cover of the cells during anode effects, may contribute to the low phosphorus content in the metal.

Anode change

Metal analysis showed that the phosphorus content decreased significantly during changing of anodes. In these periods the electrolyte is exposed to the atmosphere causing increased losses due to evaporation. The convection in the electrolyte and in the metal also increases, which seems to lower the phosphorus content in the metal.

Start-up

New cells are usually run at high temperature during the first few weeks of operation. It was consistently found from metal analysis of several such cells that the phosphorus content was very low right after start-up. Only when the temperature eventually decreased to below ~970 °C, the phosphorus content was found to rise above the detection limit of the analysis. The variations in electrolyte composition during the start-up period may also be of importance for the phosphorus concentration. A possible link between phosphorus and sodium in the metal cannot be excluded, and it is known that the sodium content in the aluminium is low during the start-up period.

Carbon dust

Some of the observations mentioned above may be explained by the presence of carbon dust in the electrolyte. Søderberg cells contain considerably more carbon dust than prebake cells.

Microscopic studies of carbon particles from industrial electrolytes using SEM/EDS showed an enrichment of phosphorus on the carbon.

Experiments were carried out where carbon dust skimmed from Søderberg cells and phosphorus compounds were added to an industrial prebake cell. It was found that the addition of carbon dust was followed by a small increase of the phosphorus content in the bath. In two experiments, silica, iron oxide and manganese oxide were added together with phosphorus. The impurities were added through the feeder holes in the centre channel of the cell. Samples were taken from the bath and the metal for analysis. Two and a half hour after the addition of impurities, carbon dust was added. Samples of particulates in the process gas during the experiments showed low contents of phosphorus.

Previous experiments have shown that after an addition the time until a homogeneous concentration in the bath is reached is about one hour. It is therefore not possible to measure the initial concentration of P in the bath. However, assuming that all of the impurities added enters the bath, i.e. nothing escapes directly into the process gas, one can calculate the initial bath concentration.

Figure 6 shows the concentrations of P in the bath and metal as a function of time after the addition. The calculated initial concentration, at time equal to zero, is also given in the figure.

The concentration in the bath immediately started to decrease, resulting in an increase of the concentration in the metal. The concentration in the metal increased to a new and higher level within two hours.

The results indicate that after the addition of carbon dust the mass transport of phosphorus from bath to metal was strongly retarded.

Some phosphorus adsorbed on small carbon particles may escape the cell with the anode gas. It is known that more carbon dust is formed during periods with increased bath temperature.
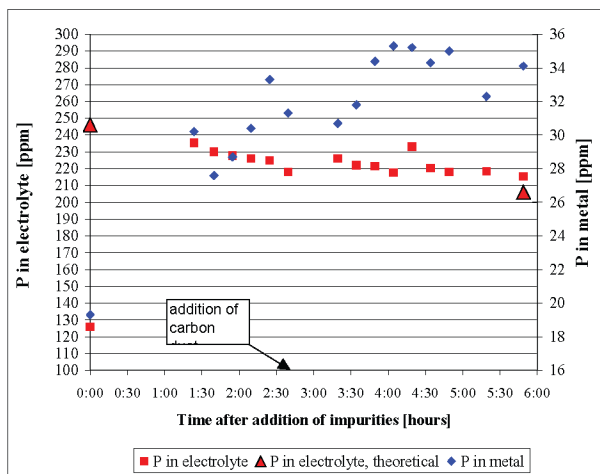

Figure 6: Concentrations of phosphorus in the bath and metal as a function of time after addition of phosphate. Carbon dust was added after two and a half hours.

Mass balance

Figure 7 show the mass flows of phosphorus for an electrolysis line with dry scrubber. The numbers indicate the phosphorus contents in the different mass flows for a typical prebake line at Hydro Aluminium, Årdal. The cells are fed with secondary alumina from the dry scrubber. The anodes are covered with a mixture of crushed electrolyte and alumina. Covering material and solidified electrolyte leave the cell when an anode is changed.
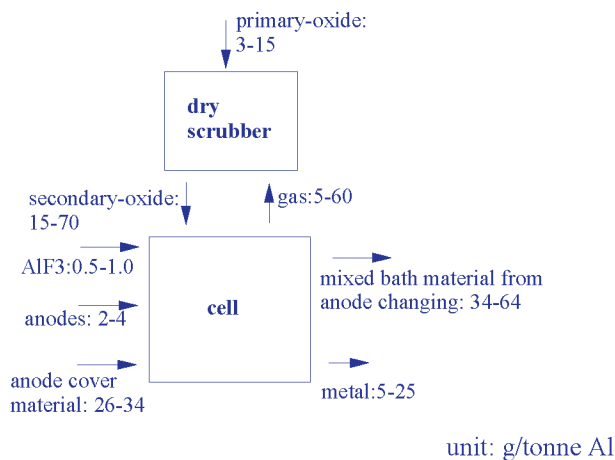

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Figure 7: Mass flows of phosphorus. The phosphorus content of the different mass flows for a typical prebake Hydro Aluminium line is given.

The difference in phosphorus concentration between primary and secondary alumina depends on the amount of P escaping from the cell with the process gas. High temperature and high concentration of carbon dust in the electrolyte result in an increased amount of P escaping the cell with the process gas or with the covering material.

Most of the phosphorus in the process gas will be collected in the dry scrubber and fed back to the cell with the secondary alumina. Also the phosphorus in the covering material and in the electrolyte removed during anode changing is fed back to the cells as new covering material. If less phosphorus leaves the cell with the aluminium than enters with the raw materials, there may be a gradual build up of P in the system. The results indicate that about 80% of the phosphorus entering the process with primary alumina end up in the metal.

Mechanism for the behaviour of phosphorus in the Hall-Heroult process

Based on the results presented from laboratory and industrial measurements and on literature data the following tentative mechanism can be proposed for the behaviour of phosphorus impurities in the Hall-Heroult process.

1. Phosphorus enters the process with the alumina probably in the form of P_2O_5 or $AlPO_4$, which dissolve in the bath as a P(V) species.

2. This species is being reduced at the cathode to gaseous elemental phosphorus. Only a small portion of the phosphorus will alloy with aluminium, since gaseous phosphorus will have a strong tendency to escape. Elementary phosphorus will be oxidised by dissolved CO_2 in the bath or at the anode. Subsequent reduction and oxidation of phosphorus compounds cause a loss in current efficiency with respect to aluminium.

3. Dissolved P(V) species may also be reduced by impurities in the bath. Small carbon particles (carbon dust) may act as nucleation sites. Phosphorus and phosphorus compounds escape with the exit gas and are being recycled back to the cells with the secondary alumina.

4. Evaporation of phosphorus compounds takes place only to a minor degree. Loss of phosphorus from the cells is mainly due to evaporation of gaseous elemental phosphorus and phosphorus attached to carbon dust. A certain amount of phosphorus may be lost to the atmosphere with small carbon particles. About 80% of the phosphorus entering the process with primary alumina end up in the metal.

5. Increased temperature leads to increased evaporation of phosphorus and reduced phosphorus content in aluminium.

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