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## Inhibition of hydrogen evolution in aluminium-phosphate refractory binders

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### Abstract

The study deals with the possibilities of inhibition of the reaction of aluminium-phosphate binders with iron scale, which is contained in bauxite. This material is mixed with phosphate binders to form refractories. The hydrogen is produced by this reaction causing the mixture foaming. The amount of evolved hydrogen was observed by the measuring by the Jank's calcimeter. Also the shape of oxidation-reduction potential of the binders was measured before and after mixing with aggregate using potentiometer. The influence of the addition of various cations on the hydrogen evolution and on the oxidation-reduction potential was observed. The effectiveness of the inhibitors was studied also visually by forming test elements.

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*Keywords:* Phosphate binder; bauxite; refractories; wear iron; inhibition; calcimeter; potentiometer

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### 1. Introduction

High alumina ceramics are preferred materials for number of reasons. Their strength is valuable for high load bearing applications, and they are resistant to corrosion in high temperature environments such as steam and CO atmospheres. Alumina ceramics are also well known for their low electrical and thermal conductivity. Therefore they are most useful materials in refractory bricks and electrical insulating components. Because of their technological importance, their low-temperature processing by chemical bonding has considerable technological significance. Phosphate bonded alumina ceramics consist of particles, whose surfaces are coated with berlinite

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(AlPO<sub>4</sub>), a crystalline orthophosphate. The bonding phase AlPO<sub>4</sub> is formed by the reaction between the phosphoric acid and alumina. This phase is a solid formed by covalent network of oxygen-bridged alternating PO<sub>4</sub> and AlO<sub>4</sub> tetrahedra. This structure is isomorphous with that of various forms of silica. Consequently, aluminium phosphate shares many chemical and physical properties of silica, yet AlPO<sub>4</sub> is formed at a much lower temperature. This lower temperature formation of AlPO<sub>4</sub>, possibly with less internal stresses in it that sintered counterparts, may translate into an economic advantage in producing ceramics suitable for high temperature service at low processing costs. [1]

Aluminium phosphate ceramics is often prepared by using an excess of acid because the solubility of alumina in phosphoric acid is highest in ultra-acidic mediums (pH<2) [1]. The abundant acid reacts with wear iron, which is contained in refractory filler (e.g. bauxite) which was milled in steel ball mills. Hydrogen is produced by this reaction, which negatively affects the shape of final products.

Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms and multiple bonds or aromatic rings, which allow an adsorption on the metal surface through lone pairs of electrons and/or pi electrons present in these molecules [2,3]. The inhibition efficiency increases in the order O < N < S < P [3]. The mechanism of the adsorption mainly follows Langmuir adsorption isotherm [2,3,4,5,6,7] or Temkin adsorption isotherm [8,9]. Some nitrogen containing heterocyclic compounds adsorb by the mechanism of simple chemisorption [10,11]. Extracts of some plants, e.g. Zenthoxylum alatum [12] or Coriandrum sativum [13], also showed themselves as good inhibitors.

Another possible method of inhibition consists in an addition of inorganic ions with positive standard electrode potential. The relation between standard electrode potential (E<sub>0</sub>) and reduction potential of a half-cell (E) is described by Nernst equation (Eq. 1):

$$E = E^0 - \frac{RT}{|z|F} \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} \quad (1)$$

where R is the universal gas constant (R = 8,314 J·K<sup>-1</sup>·mol<sup>-1</sup>); T is absolute temperature; z is the number of moles of electron transferred in the cell reaction of half-reaction; F is the Faraday constant, the number of Coulombs per mole of electrons (F = 9,649·10<sup>4</sup> C·mol<sup>-1</sup>) and a are activities of products (C, D) and reactants (A, B) raised to a higher power by their stoichiometric coefficients (a, b, c, d,) [14].

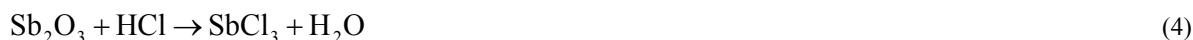
This paper is focused on a comparison of inhibiting activity of Cu<sup>2+</sup>, Ag<sup>+</sup>, Bi<sup>3+</sup> and Sb<sup>3+</sup> cations which were added in a form of suitable compounds (chlorides, nitrates, and citrates).

## 2. Materials and methods

### 2.1 Materials

First of all the phosphate binder was prepared. The solution of phosphoric acid was prepared by mixing 300 cm<sup>3</sup> of H<sub>3</sub>PO<sub>4</sub> with 150 cm<sup>3</sup> of distilled water. Then 114.1 g of Al(OH)<sub>3</sub> was dissolved in this solution. Finally, additional 5 cm<sup>3</sup> of an acid was added. The product was diluted with distilled water to the final volume of 800 cm<sup>3</sup> and filtered through Büchner funnel. The filtrate was poured into a volumetric flask and diluted with distilled water to 1 dm<sup>3</sup>.

It was necessary to choose inhibitors with both cation and anion having positive standard electrode potential. For this study CuCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Cu<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> (copper(II) citrate), AgCl, AgNO<sub>3</sub>, Ag<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, BiCl<sub>3</sub>, Bi(NO<sub>3</sub>)<sub>3</sub>, BiC<sub>6</sub>H<sub>5</sub>O<sub>7</sub> and SbCl<sub>3</sub> were chosen as inhibitors. Some inhibitors (AgCl, BiCl<sub>3</sub> and SbCl<sub>3</sub>) needed to be prepared in laboratory (Eq. 2, 3, 4):



$\text{BiCl}_3$  and  $\text{SbCl}_3$  were not isolated due to their bad chemical stability but they needed to be used in a form of chlorides prepared in slight excess of HCl.

## 2.2 Inhibiting effectiveness monitoring

Inhibiting activity of all inhibitors was studied by hydrogen evolution comparison. Jank's calcimeter was chosen for this purpose. 10 cm<sup>3</sup> of binder mixed with a required dosage of inhibitor was mixed with 0.2 g of powder iron and after 10 min the value on the calcimeter scale was read. The effectiveness of inhibitor ( $E$ ) was calculated according to an Eq. 5.

$$E = \frac{V_n - V_i}{V_n} \cdot 100 \quad (5)$$

where  $V_n$  is hydrogen evolution in pure binder and  $V_i$  is hydrogen evolution in inhibited binder.

Suitable compounds were selected for concentration dependence measuring with 20 cm<sup>3</sup> of binder and 0.5 g of powder iron (model system) and based on these results two inhibitors in suitable dosage were selected for tests in system consisting of binder and commercial filler (real system). These tests consisted of hydrogen evolution comparison and potentiometric measurements. The amount of commercial filler for hydrogen evolution comparison tests was chosen 30 g due to capacity limit of the calcimeter. The inhibiting activity of these two inhibitors was also compared by visual observation of mixture foaming when 20 cm<sup>3</sup> of binder was mixed with 80 g of commercial bauxite filler and a cup was filled with this mixture.

## 3. Results and discussion

First of all comparison of all inhibitors was done (Table 1). The weights of inhibitors were chosen so that amounts of substance ( $n$ ) of inhibitors with identical anion were consistent. At the same time it was necessary to choose as low weights as possible due to both their solubility in a binder and economic reasons.

Table 1. Comparison of the effectiveness of inhibitors.

Compound	Weight (g)	$n_{\text{cation}}$ (mmol)	$n_{\text{anion}}$ (mmol)	$E^0_{\text{cation}}$ (V) 0	Hydrogen evolution (a.u.)	Inhibition effectiveness (%)
Blank	–	–	–	–	0.74	0.00
$\text{Cu}_3(\text{C}_6\text{H}_5\text{O}_7)_2$	0.075	0.401	0.262	0.345	0.72	2.70
$\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$	0.135	0.788	0.264	0.800	0.42	43.24
$\text{BiC}_6\text{H}_5\text{O}_7$	0.106	0.264	0.264	0.320	0.92	-24.32
$\text{CuCl}_2$	0.098	0.571	1.161	0.345	0.61	17.57
$\text{AgCl}$	0.162	1.126	1.142	0.800	0.59	20.27
$\text{BiCl}_3$	0.120	0.379	1.151	0.320	0.78	-5.41
$\text{SbCl}_3$	0.086	0.374	1.140	0.152	0.22	70.27
$\text{Cu}(\text{NO}_3)_2$	0.098	0.417	0.830	0.345	0.20	72.97
$\text{AgNO}_3$	0.135	0.801	0.784	0.800	0.32	56.76
$\text{Bi}(\text{NO}_3)_3$	0.109	0.276	0.826	0.320	0.53	28.38

Solubility was the main problem in a usage of some inhibitors. Attempts to improve their solubility were realized by an addition of an acid (HCl in the case of AgCl, HNO<sub>3</sub> in the case of Bi(NO<sub>3</sub>)<sub>3</sub>) but these additions showed themselves as insufficient or even disserviceable.

CuCl<sub>2</sub>, BiCl<sub>3</sub>, SbCl<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> and AgNO<sub>3</sub> were selected for concentration dependence measuring. All these compounds were relatively well soluble in the binder. As you can see in Fig. 1, lower amount of both Bi<sup>3+</sup> and Sb<sup>3+</sup> is needed to reach maximum inhibition effect than Cu<sup>2+</sup>. The difference between inhibition effectiveness of Bi<sup>3+</sup> and Sb<sup>3+</sup> is minimal. Cu<sup>2+</sup> already reaches high inhibition effectiveness by low concentration but Ag<sup>+</sup> is able to reach higher inhibition effectiveness than Cu<sup>2+</sup>. Moreover Cu<sup>2+</sup> showed one more disadvantage; addition of these ions in each concentration turned the binder into blue.

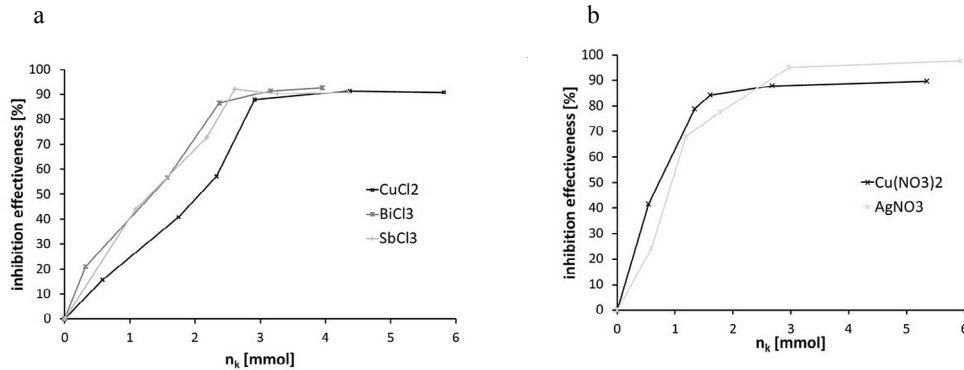


Fig. 1. Comparison of inhibition effectiveness of individual cations (a) chlorides; (b) nitrates.

For measurement in real system 0.3 g of AgNO<sub>3</sub> and 0.6 g of SbCl<sub>3</sub> were selected. The main criterion for inhibitor selection was maximum inhibition effectiveness reaching by minimum amount of inhibitor. It is also suitable to use inhibitor which would not influence the colour of the binder. The comparison of these two inhibitors by hydrogen evolution measuring both for model and real system is shown in Fig. 2. The addition of 0.6 g of SbCl<sub>3</sub> was found to be more suitable in both systems. The difference in effectiveness of inhibition of both inhibitors was demonstrably lower in real system.

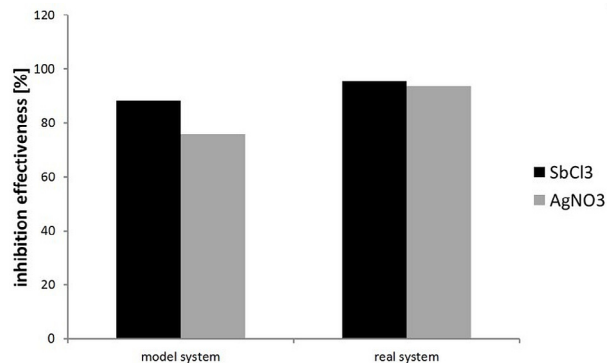


Fig. 2. Inhibition effectiveness measurement in model and real system.

Fig. 3 represents the potentiometric measurement results. An addition of AgNO<sub>3</sub> brings the potentiometric curve to positive values whereas SbCl<sub>3</sub> addition leads to reduction potential decrease. This phenomenon could have been caused by the excess of HCl in SbCl<sub>3</sub> solution which also could have reacted with powder iron. Measurement in real system confirmed the suitability of AgNO<sub>3</sub> addition. Not only the reduction potential mainly ranged in positive

values but also the time of a step lowering of reduction potential was substantially delayed (more than 4 minutes). In contrast to model system measuring also  $\text{SbCl}_3$  lead to reduction potential increase. The excess of  $\text{HCl}$  has not so important influence on reduction potential when using commercial bauxite filler in contrast to measurement with powder iron.

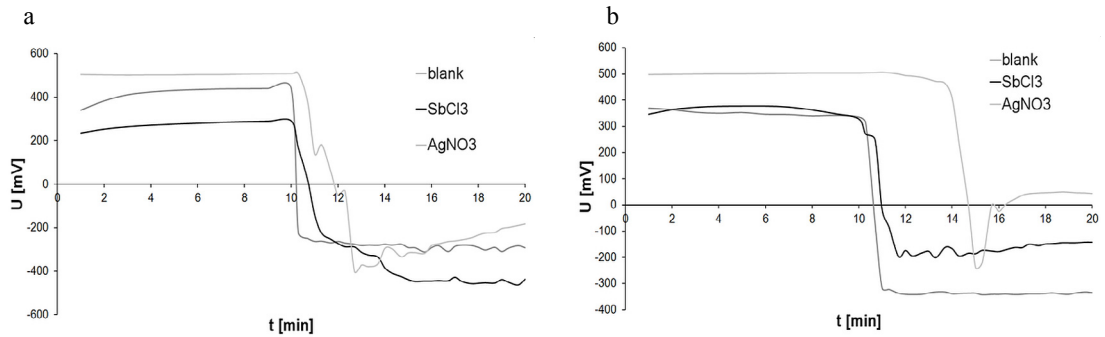
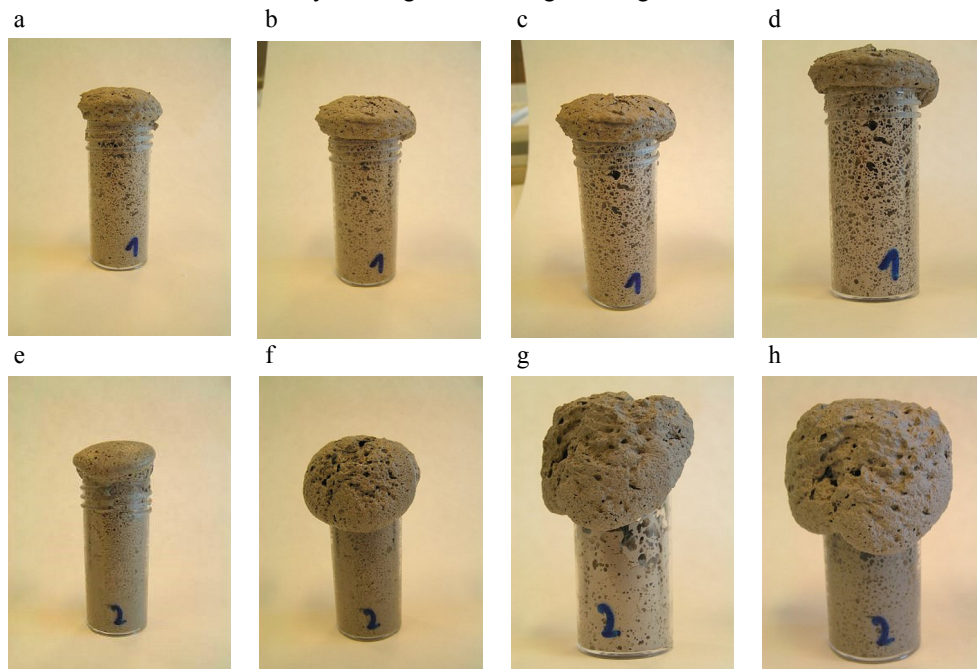


Fig. 3. Time voltage dependence measuring of non-inhibited binder and binder inhibited with 0.3 g of  $\text{AgNO}_3$  and 0.6 g of  $\text{SbCl}_3$  in (a) model system; (b) real system.

Binder without inhibitor addition, binder mixed with 0.6 g of  $\text{SbCl}_3$ , binder mixed with 0.3 g of  $\text{AgNO}_3$  and binder mixed with 0.6 g  $\text{SbCl}_3$  prepared in an excess of  $\text{HCl}$  were used for visual observation of inhibition activity. Fig. 4 indicates that as  $\text{AgNO}_3$  showed significant inhibition activity,  $\text{SbCl}_3$  did not prevent hydrogen evolution despite promising outputs of hydrogen evolution measuring at Jank's calcimeter. The most verisimilar reason for difference between outputs of these two tests lies in usage of more than double amount of commercial bauxite filler for visual observation test. Selected amount of  $\text{SbCl}_3$  is probably sufficient for inhibition of reaction of binder with iron contained in 30 g of filler but not for inhibition of reaction with excess contained in 80 g of filler.  $\text{AgNO}_3$  in comparison with  $\text{SbCl}_3$  was effective by the usage of both 30 g and 80 g of filler.



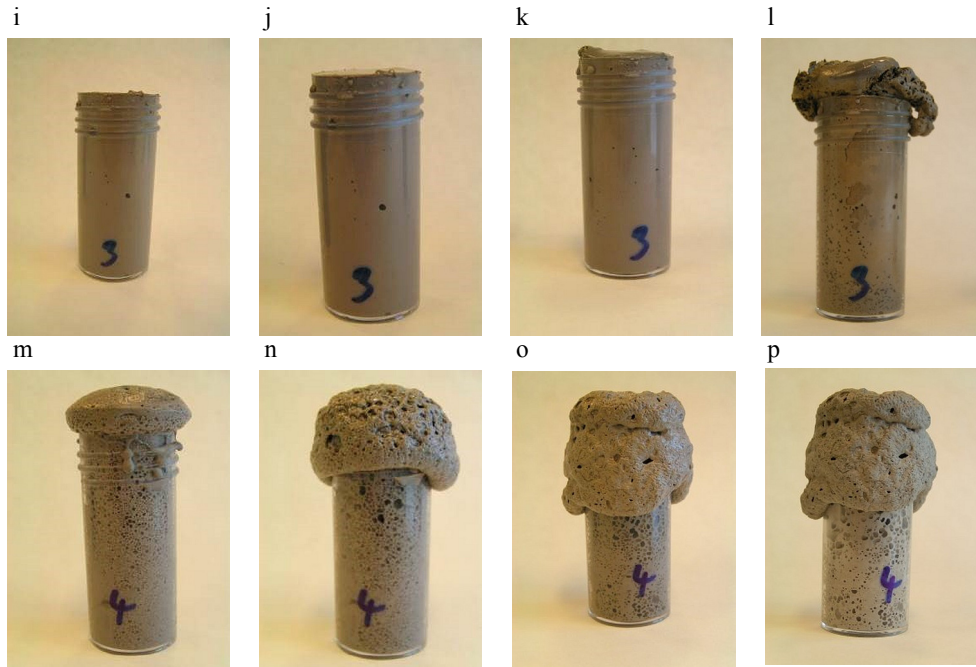


Fig. 4. Mixture of binder (a-d) non-inhibited after (a) 5 min; (b) 10 min; (c) 60 min and (d) 24 hours; (e-h) with an addition of 0.6 g of  $\text{SbCl}_3$  after (e) 5 min; (f) 10 min; (g) 60 min and (h) 24 hours; (i-l) with an addition of 0.3 g of  $\text{AgNO}_3$  after (i) 5 min; (j) 10 min; (k) 60 min and (l) 24 hours and (m-p) with an addition of 0.3 g of  $\text{SbCl}_3$  in an abundance of  $\text{HCl}$  after (m) 5 min; (n) 10 min; (o) 60 min and (p) 24 hours.

#### 4. Conclusion

Influence of  $\text{Cu}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Sb}^{3+}$  and  $\text{Ag}^+$  on hydrogen evolution in aluminum phosphate binders after mixing with powder iron or iron containing filler was studied. Cations were added in a form of chlorides, nitrates and citrates. In these work 10 compounds were compared and concentration dependences were plot for 5 of them. Two inhibitors were tested in a real system.

Copper (II) compounds showed very good solubility in the binder, moreover they are cheap and easily available in comparison with compounds of other observed cations. On the other hand maximum inhibition effectiveness of these compounds is not as high (especially in comparison with  $\text{Ag}^+$  compounds) and these compounds tend to turn the color of the binder into blue.

Silver compounds did not change the color of the binder when used in concentrations sufficient for high inhibition effectiveness; moreover the addition of these compounds enabled us to reach more than 95 % inhibition effectiveness. The suitability of these inhibitors was testified by experiments in real system. However, silver compounds are relatively badly soluble in the binder and in comparison with copper (II) compounds they offer lower scale of suitable salts. Another limiting factor of the usage of these inhibitors lies in their high cost.

Bismuth (III) and antimony (III) compounds also do not cause the change of color of the binder and compared to previous two ions they showed significant inhibition ability already by lower amounts of substance. These compounds, however, lead to the creation of a white opacity just by low concentrations. Similarly their poor solubility belongs to their considerable disadvantages. Their chlorides are partly soluble but they are commercially badly accessible so they need to be prepared in an abundance of  $\text{HCl}$  which has a negative influence on the inhibition of the reaction of binders with iron. Both potentiometric measurement and visual testing testified against antimony (III) compounds in comparison with silver ones.

The main topic for following research could be focused at finishing and describing the influence of cations, to examine the influence of anions (some research on this topic was carried out by another colleague). It would be also

appropriate to carry out morphological and microscopic tests of iron scale, eventually on model iron surface. The optimization of inhibitor dosing and possible stabilization of the mixture would be also important research area. After potential transfer of technology to industrial scale it would be interesting to solve an optimization of technology to the intent of the conditions of mixing binder with filler or in the relation with corrosion properties of the binder.

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