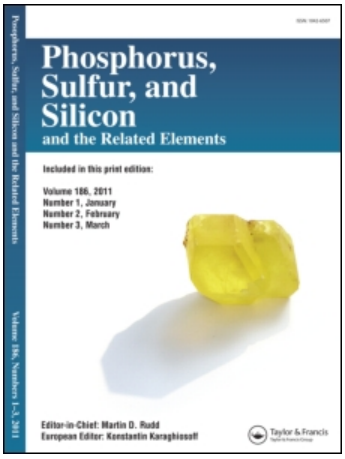

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Kuzmenkov, M. I. and Goldar, T. E.(1987) 'Synthesis and Studies of Aluminium Chlorophosphates', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 437 — 442
To link to this Article: DOI: 10.1080/03086648708080614
URL: http://dx.doi.org/10.1080/03086648708080614

Phosphorus and Sulfur, 1987, Vol. 30, pp. 437-442
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SYNTHESIS AND STUDIES OF ALUMINIUM CHLOROPHOSPHATES

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On the base of aluminium, chromium, and alumochromiumphosphate binders, the efficient uncalcined refractory materials, glues, thermo- and electroinsulating materials that feature a high thermal stability have been obtained and applied. However, in these binders the atomic phosphorus/metal ratio is to be no less that 3 for individual and 2.3 for the mixed binders on cation to have them stable on storage which specifies a number of their technological shortcomings.

The introduction of chlorine anions into a binder composition permits obtaining the solutions stable to crystallization for a long time at the phosphorus/metal ratio equal to a unity and the addition to composites will simplify their technology and improve their quality [1,2].

The powdered "Winnofos" ICI-binders - complex aluminium phosphates containing a chlorine ion - and different methods of its preparation were described in literature. However, the compressive strength of refractory concretes on their base does not exceed 16.8 MPa at 110°c, 37.5 MPa at 500°C and 24.9 MPa at 1000°C [3.]

The aim of this work was to study the formation conditions, composition, and properties of aluminium

and chromium chlorophosphates used as a binder in the form of a viscous solution and a powdered product isolated from it.

The above chlorophosphate binders provide a higher mechanical strength and thermal stability of the composites on their base as well as make it possible to lower the temperature of their preparation.

The synthesis of aluminium and chromium chlorophosphates involves two stages:

(1) Interaction between a metal-containing component and orthophosphoric and hydrochloric acids at the M:P:CL=1:1:1.2-1.8 ratio followed by the solution evaporation to obtain a viscous binder.

(2) Isolation of a powdered product by crystallization, salting-out with acetone or drying [1,2,4].

The interaction is carried out by one of the following reactions:

$$\{AlCl_3\}aq + H_3PO_4 \rightarrow \{AlHPO_4Cl\}aq + 2HCl \quad (1)$$

$$Al(OH)_3 + H_3PO_4 + HCl \rightarrow \{AlHPO_4Cl\}aq + 3H_2O \quad (2)$$

$$\{AlCl_3\}aq + 2H_3PO_4 + Al(OH)_3 \rightarrow 2\{AlHPO_4Cl\}aq + 3H_2O + HCl \quad (3)$$

$$\{CrCl_3\}aq + H_3PO_4 \rightarrow \{CrHPO_4Cl\}aq + 2HCl \quad (4)$$

$$Cr(OH)_3 \cdot 2H_2O + H_3PO_4 + HCl \rightarrow \{CrHPO_4Cl\}aq + 5H_2O \quad (5)$$

$$\{CrCl_3\}aq + 2H_3PO_4 + Cr(OH)_3 \cdot 2H_2O \rightarrow 2\{CrHPO_4Cl\}aq + 5H_2O + HCl \quad (6)$$

The aluminium-containing product is a colourless transparent solution of the 1.58-1.63 g/cm^3 density. Its viscosity is 4.9 - 16.1 Pa.s, concentration is 48-54% in terms of $AlHPO_4Cl$, with the atomic P:Al=1 ratio. It features a good adhesive ability and does not crystallize within three months.

The chromium-containing binder is a green solution of the 1.60-1.64 g/cm^3 density. Its viscosity is 0.28-4.64 Pa•s, concentration is 50-52 in terms of $CrHPO_4Cl$ with the atomic P:Cr=1 ratio. It does not crystallize for more than a year.

An identical crystalline water-soluble product, aluminium chlorophosphate, was isolated from the solution obtained by reaction (1-3), by crystallization or salting-out with acetone. By its chemical composition, it corresponds to the formula $AlHPO_4Cl \cdot 4H_2O$ whose X-ray pattern and IR-spectrum do not coincide with those know for the complex aluminium phosphates [5-6].

An amorphous, insoluble product - chromium chlorophosphate - however, dispersing in water into fine particles, was isolated from the solution obtained according to reactions (4-6) by drying in the air or in vacuum. By its chemical composition, it corresponds to the formula $CrHPO_4Cl \cdot 6H_2O$. Its IR-spectrum differs from those know for chromium phosphates.

The electron microscopic confirm that the aluminium chlorophosphate crystallizes in the form of 1-3 mcm plates and has amorphous nature.

The thermal transformations of binders have been studied by the DTA, IRS, X-ray, and paper chromatography methods.

The aluminium and chlorophosphates are thermally un stable compounds and transform into anhydrous orthophosphates by a different mechanism.

There are two endoeffects with minima at 110°C and 160°C corresponding to the removal of one mole

of hydrogen chloride and four moles of hydrate water in the derivatogram of aluminium chlorophosphate taken at the heating rate of 5 drade/min. The isothermal studies showed a removal of 1 mole of H_2O and almost a complete removal of HCl at 110°C; after 2 hr of keeping 3.9% Cl is removed; after 8 hr, 14.0% Cl and after 10 hr a complete removal of 15.4% Cl occurs that contained in the starting sample. A substantially higher endoeffect with a minimum at 160°C corresponds to the final product dehydration. In this case, keeping the sample within 1 hr results in a complete transfer into an amorphous state follwed after 2 hr by crystallization of an amorphous intermediate phase into the anhydrous aluminium orthophosphate, $AlPO_4$, of the tridymite modification. The losses upon calcination of aluminium chlorophosphate up to 1000°C amount to 49.0%, which corresponds to the theoretical $AlHPO_4Cl \cdot 4H_2O$ loss: 1 mole of HCl; 4 mole of H_2O (46.9) and 2.1% of adsorbed moisture. Keeping the sample for 6 hr at 1400°C results in the polymorphous transformation of the tridymite from into a cristobalite one.

The chromium chlorophosphate decomposition involving removal of gaseous products proceeds through four stages and is accompanied by endoeffects with minima at 80°C, 150°C,and 920°C and exoeffects with maxima at 450°C and 940°C corresponding to the formation of new phases. In this case, the chlorophosphate and the products of its thermal treatment remain amorphous to about 800°C. In the sample kept within 2 hr at 80°C, only 1.3% of its starting content (12.1%) is left, i.e. the chlorine

ion bond in the chromium chlorophosphate is less strong than in the aluminium chlorophosphate. After a mole of HCl is lost at 80°C a further transformation of the chromium chlorophosphate follows the $CrPO_4 \cdot 6H_2O$ dehydration, the $CrPO_4 \cdot 4H_2O$ and $CrPO_4 \cdot O \cdot 5H_2O$ being present as intermediate phases as evidenced by the losses upon calcination. The endoeffect at 920°C corresponds to the loss of the last 0,5 mole of water and the β-$CrPO_4$ crystallization transforming into α-$CrPO_4$ at 940°C whose melting temperature is 1800°C. The total losses upon calcination amount to 52.3% which corresponds to the theoretical loss of a mole of HCl, 6 moles of H_2O (49.6%) and 2.7% of adsorbed water.

The thermal transformation mechanism of aluminium and chromium chlorophosphates can be represented as follows:

$$\underset{\text{crystalline}}{AlHPO_4Cl \cdot 4H_2O} \xrightarrow[-HCl,\,-4H_2O]{80\text{-}160^\circ C} \underset{\text{amorphous}}{AlPO_4} \xrightarrow[2hr]{160^\circ C} x$$

$$x\ AlPO_4 \xrightarrow[6\ hr]{1400^\circ C} \underset{\text{cristobalite}}{AlPO_4}$$
tridymite

$$\underset{\text{amorphous}}{CrHPO_4Cl \cdot 6H_2O} \xrightarrow[-HCl,\,-2H_2O]{50\text{-}200^\circ C} \underset{\text{amorphous}}{CrPO_4 \cdot 4H_2O} \xrightarrow[-3.5H_2O]{450^\circ C}$$

$$\underset{\text{amorphous}}{CrPO_4 \cdot O \cdot 5H_2O} \xrightarrow[-0.5H_2O]{920^\circ C} \underset{\text{crystalline}}{\beta\text{-}CrPO_4} \xrightarrow{940^\circ C} \underset{\text{crystalline}}{\alpha\text{-}CrPO_4}.$$

The formation of thermally stable orthophosphate as the only final products of thermal transformations of aluminium and chromium chlorophosphates permitted a number of heat-resistant composites

of considerable strength to be prepared on their base (σ_{comp} to 60 MPa for alumo- and σ_{comp} to 78 MPa for chromium-chlorophosphate binder) produced by moulding and at the hardening temperature of 200°C [1,4,7,8].

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