

THE INVESTIGATION OF POSSIBILITIES OF MONO AL PHOSPHATE AND AlCr PHOSPHATE SYNTHESIS – THE BINDERS FOR REFRACTORIES

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ABSTRACT

The whole work is part of doctoral dissertation mr. sc. Nadira Bušatlić under the supervision of prof. dr. Petar Petrovski titled: „ The effect of metakaolin on the preparation and properties of refractory materials with phosphate binders“. In the industry of refractory materials for the preparation of chemically bonded refractory materials (concretes and monoliths) various phosphates are used. As a phosphate binder 50 % solution of mono aluminium phosphate, $Al(H_2PO_4)_3$ is the most commonly used, which is resulted by neutralization of the first H^+ ions from phosphoric acid with $Al(OH)_3$. If a mono aluminium phosphate is further neutralized with Cr_2O_3 then AlCr phosphate is occurred. The purpose of this study was to investigate the possibility of synthesis of two leading phpsphate binders which are used in the indusry of refractories: mono aluminium phosphate and aluminium chrome phosphate.

Keywords: mono aluminium phosphate, AlCr phosphate, refractory materials, phosphate binders

INTRODUCTION

In the industry of refractory materials for the preparation of chemically bonded refractory materials (concretes and monoliths) various phosphates are used. As a rule, these phosphates are added to refractory aggregates (quartz, fireclay, mullite, corundum, etc.) as aqueous solutions. Mono aluminium phosphate (40 – 50 % aqueous solutions), ammonium phosphate, chrome aluminium phosphate, alkaline meta and poly phosphate are in the application. The stability of the mass of the binding depends on the ratio of $X = P_2O_5 : Al_2O_3$. Stability is increased when the mass is more acid. It is even metastable at $X = 3$, and when $X = 2,3$ or less, precipitation is occurred and then curing [1]. Hardening alumosilicate products by binding phosphate is conditioned by formation of acid phosphates, by their polymerization and polycondensation in the process of heating, and also by formation of insoluble phosphate in reaction of phosphoric acid with the oxides of the refractory fillers.

The acidic phosphates $AlH_3(PO_4)_2 \cdot 3H_2O$, $Al(H_2PO_4)_3$ and $Al(HPO_4)_3$ don't have the same significance for phosphate binding. The most important is mono Al phosphate, which achieve phosphorus (chemical) bonding in the temperature range from 100-300 ° C. Further heated to 800 ° C hydrate acid phosphate, which is created dominantly in the first time, as well as mono Al phosphate they gradually dehydrate and created bond gradually becomes from a chemical into ceramic. Phosphate hydrate gives tridimit form of $AlPO_4$ and Al mono phosphate becomes metaphosphate $Al(PO_3)_3$. At a temperature of 1021 ° C tridimit form of phosphate becomes cristobalite one. At a temperature of 1500 ° C metaphosphate is decomposed into cristoballite $AlPO_4$ and P_2O_5 . $AlPO_4$ is stable until the temperature of 1760 ° C, when it is decomposed into (refractory) Al_2O_3 and P_2O_5 . [2]

As a phosphate binder 50 % solution of mono aluminium phosphate, $Al(H_2PO_4)_3$ is the most commonly used, which is resulted by neutralization of the first H^+ ions from phosphoric acid with $Al(OH)_3$. If a mono aluminium phosphate is further neutralized with Cr_2O_3 then AlCr phosphate is occurred. For the preparation of refractory materials phosphoric acid, monoaluminium phosphate and aluminium chrome phosphate are mainly used. If phosphoric acid is neutralized with Cr^{3+} (alone or with other cations), then very stable solutions of chrome phosphate with better colloidal properties are occurred (binders with better quality then phosphoric acid and mono aluminium phosphate).

The purpose of this study was to investigate the possibility of synthesis of two leading phosphate binders which are used in the industry of refractories: mono aluminium phosphate and aluminium chrome phosphate [3].

1. SYNTHESIS OF PHOSPHATE BINDERS, MONO ALUMINIUM PHOSPHATE AND ALUMINIUM CHROME PHOSPHATE

Synthesis of both phosphate was performed starting from different reagents which are:

- Holders of chromium: a) chromium oxide Cr_2O_3 and CrO_3 ; b) Potassium dichromate; c) Chromium hydroxide; d) Chromium chloride;
- Holders of aluminum: a) Elemental Al, foil and powder; b) Aluminium chloride; c) aluminum hydroxide
- The holders of phosphorus: a) Phosphoric acid.

As we did not have a commercial chromium hydroxide and chromium chloride, synthesis of the same ones was done in the following way:

Chromium chloride, was obtained by dissolving Cr_2O_3 on hot in concentrated HCl. Also, chromium chloride can be obtained starting from CrO_3 by heating a mixture of CrO_3 and HCl (HCl has reducing effect).

Chromium hydroxide was obtained by precipitation from solution of chromium chloride with ammonia. The precipitate was filtered off and air-dried.

Synthesis of mono aluminium phosphate and aluminium chrome phosphate was performed in a simple apparatus which consisted of reaction balloons from 250 ml with a reflux condenser and magnetic stirrer. Reaction balloon was heated on hot plate (Figure 1.) [4].

1.1. PREPARATION OF MONO ALUMINIUM PHOSPHATE

Mono aluminium phosphate was prepared as a 30 % and 50 % solution. Dissolving of Al trihydrate in concentrated H_3PO_4 is difficult. As time progresses the solution becomes more viscous so that it is practically impossible to mix. Therefore, we dissolved the trihydrate in dilute acid; the addition of water is such that by dissolving of Al trihydrate it is prepared 30% or 50% solution monoaluminium phosphate which contains unrelated H_3PO_4 .

On the basis of tests optimal conditions for the preparation of mono Al phosphate solution can be determined:

The starting components:

$\text{Al}(\text{OH})_3$, purity 94 %	_____	79 g
Concentrated H_3PO_4	_____	224 ml
Water	_____	180 ml

Requirements:

Temperature _____ about 100 °C

Time _____ 2 hours.

The result: about 500 ml of 50% MAP density from 1.52 to 1.53 g/cm^3 [4].

1.2. PREPARATION OF AlCr PHOSPHATE

Seven synthesis were done as follows. The characteristics of the products were determined visually and on the basis of chemical analysis.

Note: The amounts of $\text{Al}(\text{OH})_3$, carriers of Cr component (Cr_2O_3 , CrO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$), H_3PO_4 and H_2O , adjusted to the stoichiometric ratio: $1\text{Al}_2\text{O}_3$: 0.4 - 0.5 Cr_2O_3 : 3.5 P_2O_5 , which was determined by analyzing a comparable commercial sample (P_2O_5 is at approximately 10% excess) of AlCr phosphate the producer of TKI Hrastnik Slovenia (table 1). Water was added in an amount which provides the density of the solution approximate to density of a commercial sample.

Chemical composition of AlCr phosphate: Al_2O_3 7,57 %; Cr_2O_3 4,79 %; P_2O_5 31,87 %; H_2O 48,96 %.
pH = 2-3; Density 1,465 g/cm^3

Synthesis no. 1

About 0.5 g of fine powdered Cr_2O_3 was added slowly to 25 ml of concentrated H_3PO_4 (85%) with vigorous stirring. The mixture was heated to boiling and kept like that for about 2 hours, and then 1 g of powdered Al trihydrate was slowly added. Dissolving lasted approximately for one hour. Over time, the solution becomes viscous, so that the mixing is difficult. After cooling, the highly viscous

solution becomes almost solid, and it is evident that contains undissolved particles of Cr_2O_3 and $\text{Al}(\text{OH})_3$.

Synthesis no. 2

Approximately 0.5 g of fine powdered Cr_2O_3 was dosed in a few servings into heated solution of previously prepared mono Al phosphate, with vigorous stirring. However, despite the long-term dissolution at the boiling point of the solution, Cr_2O_3 powder was not substantially dissolved.

Synthesis no. 3

About 3 g of fine powdered $\text{Al}(\text{OH})_3$ was mixed on a cold with dilute H_3PO_4 , 60% solution, and then the mixture was heated by stirring at boiling temperature until complete dissolution of the trihydrate. Then about 1 g of solid anhydrous CrCl_3 was added which was completely dissolved. Viscous sticky dark green of liquid was obtained, solution of AlCr phosphate with an excess of unbound H_3PO_4 .

Synthesis no. 4

In 30 g of concentrated H_3PO_4 , 85% solution, 3.6 g of fine powdered commercial $\text{Al}(\text{OH})_3$ was added to a cold, containing 94% $\text{Al}(\text{OH})_3$ and 10 ml of water. The mixture was then heated by stirring until complete dissolution of Al trihydrate, and then in several portions 3.5 g of anhydrous dry CrO_3 was added. After complete dissolution (clear solution), reduction was carried out, transforming of Cr^{6+} to Cr^{3+} condition, and as a reducing agent sucrose was used. By adding sugar into solution the intense foaming and caramelization of sugar appear, and the solution becomes viscous, and after a while it practically solidified. It is therefore appropriate to add instead of solid, 10 - 15% sugar solution in small portions by vigorous stirring. The solution needs to be heated, and the optimum operating temperature is in the range of 50-60 °C. Time reduction is short, and we follow it by changing the color of the solution – transition of orange to green. Very viscous sticky dark green of liquid was obtained – certainly the solution of AlCr phosphate with excess unreacted H_3PO_4 .

Synthesis no. 5

About 3 g of solid CrO_3 was dissolved by stirring at room temperature in 30 g of concentrated H_3PO_4 (85% solution), and then by stirring 10% of sucrose solution was added until complete reduction of the Cr^{3+} ions in the trivalent state – transition of orange solution to green. The temperature was maintained in the range from 50 to 60 °C. A dark green solution of mono chrome phosphate was obtained containing unrelated H_3PO_4 . The solution is then heated to boiling, and by gently stirring in several portions 1.7 g of Al trihydrate was added. Dissolving of trihydrate was going very slowly. A highly viscous dark green solution of AlCr phosphate was obtained containing excess of H_3PO_4 .

Synthesis no. 6

About 3 g of solid CrO_3 was dissolved in 30 g of 60% H_3PO_4 solution at room temperature. The resulting solution was then heated to boiling. By vigorous stirring, in several portions 1.7 g of Al powder was added (Al powder has to be added in the smaller portions, because the hydrogen evolution leads to intense foaming.). A viscous dark green solution of AlCr phosphate was obtained in which we can observe particles undissolved aluminum. The previous procedure was repeated, instead of Al powder as a reducing agent fine divided Al foil was used. Reaction of the reduction in this case is much slower compared to the reduction of the powder, because after a short time in spite of the vigorous stirring, partial or complete passivation of surface pieces of aluminum foil is occurred.

Synthesis no.7

About 5 g of anhydrous $\text{K}_2\text{Cr}_2\text{O}_7$ was dissolved in 30 g of 70% H_3PO_4 . After heating the solution to boiling point with vigorous stirring 1.5 g of Al powder was added in small portions. A viscous dark green solution of AlCr phosphate was obtained containing part of undissolved aluminum powder and unrelated H_3PO_4 . It should be said that the solution contains potassium ions that are, considering the use of the product, undesirable [4].

On the basis of tests the optimal conditions for preparing AlCr phosphate can be determined:

The starting components:

50 % solution of MAP _____ 500 ml

Cr_2O_3 , purity 100 % _____ 32,5 g

20 % solution saccharose _____ 50 ml

The conditions of preparation:

Temperature _____ about 60 °C

Time of search _____ 2 hours

The density of the resulting solution is 1.52 g/cm³. Addition of water can lead density to 1.465 g/cm³ such as density of commercial product [4].

2. DISCUSSION OF RESULTS

Tests have shown that chromium (III) oxide Cr_2O_3 , both commercial and synthesized in the laboratory, can not be used in the synthesis we did. It is not dissolved or slightly dissolved, nor in concentrated H_3PO_4 , and in dilute, nor in mono aluminum phosphate solution, by heating to the boiling solution and vigorous stirring. Also chromium hydroxide is very difficult to dissolve, both in concentrated, and in dilute H_3PO_4 and after prolonged heating to boiling, stirring vigorously. It is also the same in the dissolution of previous prepared 30 or 50% solution of mono Al phosphate. Due to the presence of water the allocation of phosphate gel is appeared.

On the other hand, chromium (VI) oxide CrO_3 and chromium chloride CrCl_3 are dissolved very easily by stirring and gently warming, both in H_3PO_4 , and in solutions of 30 and 50% solution of mono Al phosphate. It is noted that CrO_3 is dissolved faster and easier in solutions of mono Al phosphate than in H_3PO_4 . Therefore we do not recommend preparing of AlCr phosphate in which CrO_3 is dissolved first in H_3PO_4 , and then $\text{Al}(\text{OH})_3$ is added. The order is reversed. (Chromium chloride is unsuitable since undesirable chlorine ions are brought in a product, the solution of AlCr phosphate).

As a starting material for the preparation of phosphate AlCr is a chrome oxide CrO_3 . In the first phase CrO_3 is dissolved in a solution of mono Al phosphate, in the final part of the synthesis it is necessary to reduce Cr^{6+} to Cr^{3+} state. As reducing agents are Al powder and foil, and sucrose. The use of aluminum powders is related to a series of problems of which are the most prominent: the creation of a cloud of fine dust during dosing, intense foaming of solution which the powder is added to because of hydrogen evolution, the long-term dissolution (formation of lumps) and lagging of undissolved powder in the product. By using of aluminum foil, in order to prevent the above deficiencies, the desired result was not achieved. Dissolution of finely comminuted pieces of foil was very slow because the material for a short time is passivated, superstructure of oxide and phosphate on the surface). An attempt was made to activate Al foil of prior treatment with mercuric chloride, but in this case the expected result was not given.

Very good results were obtained by using sucrose as a reducing agent. The reduction is rapid and complete - it is easy to follow because by the reduction the color of solution is changed: purple to green. Reaction of reduction is exothermic. Reducing agents, previously dissolved in water, are added from a dropping funnel slowly, and the solution temperature should be kept at about 60°C .

CONCLUSIONS

- Preparation of mono Al phosphate by dissolving of $\text{Al}(\text{OH})_3$ powder in dilute H_3PO_4 on hot by stirring is a simple and reliable method.
- Preparation of AlCr phosphate is certainly more complex and it is the most acceptable more process in which the starting materials are: mono Al phosphate solution and solid CrO_3 , and 10% sucrose solution, as the reducing agent.
- The resulting product does not contain ions of alkali metals or amon ion, what happens if the bichromate are used as the reagents and chloride ion in the case when the chromic chloride is a reagent, which should be taken into account with regard to the scope of application of phosphate - binders for refractory materials.

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