

# Aluminum Phosphate Phase Changes Caused by the Exposure Environment

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## Abstract

Phosphate compounds are used in refractories for severe service applications that include gasification, glass melting, and metals processing; impacting refractory material strength and corrosion resistance. The phosphate and other materials used in a refractory, material grain sizing and the porosity of the finished refractory, how a refractory is fabricated and used in service, and the furnace environment (oxygen partial pressure and temperature) influence phosphate phases formed or existing during industrial service. Data will be presented from weight and phase changes in two phosphate compounds (aluminum meta- and ortho-phosphate) and compared against thermodynamic predictions to understand refractory behavior observed during use – information that can be used to maximize refractory performance.

## 1. Introduction

Refractory materials are used by industry in high temperature severe service environments to contain a reaction, protecting the reaction chamber from wear and/or corrosion. Ceramic materials such as  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3/\text{SiO}_2$  clays,  $\text{AlN}$ ,  $\text{SiC}$ , and other oxides/carbides/ nitrides, or mixtures of them have evolved or been developed as the working lining for applications including in steel, aluminum, glass, and chemical production. Predictable service life of the hot face refractory liner is important in gasification, a process that converts a carbon feedstock (such as coal and petroleum coke) into synthesis gas (a gas mixture consisting primarily of  $\text{CO}$  and  $\text{H}_2$  used as a precursor for chemical production or that is combusted for power generation). The basic gasification reaction to produce syngas is illustrated in **Eq. 1**; which occurs in a low oxygen partial pressure environment.

### Equation 1:

$\text{C}$  (excess - typically coal, petcoke) +  $\text{H}_2\text{O}$  (added intentionally) +  $\text{O}_2$  (shortage)  $\rightarrow$   $\text{CO}$  +  $\text{H}_2$  + by-product gases (including  $\text{H}_2\text{S}$  +  $\text{CO}_2$ ) + process by-products (including slag + excess  $\text{C}$ ) + thermal energy (heat)

Additives in refractory manufacturing, such as carbon (as pitch or resin) are often made to the oxide material to bond materials or to improve material slag resistance. In gasification, phosphate additions are often made to the base high chrome

oxide composition (shown in **Table 1**) to improve spalling and corrosion resistance, resulting in longer service life<sup>1</sup>.

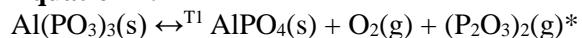
**Table 1 Chemical and physical properties of two types of refractories used in gasifiers (with/without phosphate additions).**

Refractory Type	Chemistry (wt pct)			Porosity (pct)
	$\text{Cr}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{P}_2\text{O}_5$	
Type A	90.1	9.3	NL	14.8
Type B	92.0	4.7	3.3	15.0

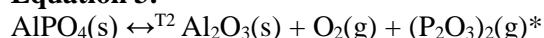
NL = Not Listed

Movement of the phosphates within and from the refractory have been noted with prolonged gasifier use<sup>2, 3</sup>. The mechanism of how phosphate phases change at elevated temperatures and over a range of low oxygen partial pressures was reported<sup>4</sup>, with two basic reactions noted (**Eqs. 2 + 3**). Changes are dependent on the starting phase of aluminum phosphate, the quantity of it, service temperature, and oxygen partial pressure. Note that the reactions are not balanced; and that **Eq. 2** indicates the thermal breakdown of aluminum metaphosphate  $[\text{Al}(\text{PO}_3)_3]$  into aluminum orthophosphate  $[\text{AlPO}_4]$ , and that **Eqs. 3** indicates the thermal breakdown of aluminum orthophosphate  $[\text{AlPO}_4]$  into  $\text{Al}_2\text{O}_3$  as measured using a controlled atmosphere thermal gravimetric analysis (TGA) - partial pressure of  $10^{-10}$  atm  $\text{O}_2$ .

### Equation 2:



### Equation 3:



$\text{T}^1$  = about 830 °C;  $\text{T}^2$  = about 1220 °C; (note both  $\text{T}^1 + \text{T}^2$  were determined in  $10^{-10}$  atm  $\text{O}_2$  pp by TGA)

\*Equations are not balanced

The breakdown temperatures of phosphate at a given oxygen partial pressure (in the example presented, an oxygen partial pressure of  $10^{-10}$  atm) were about 830 °C for the aluminum metaphosphate and 1220 °C for the aluminum orthophosphate, with gaseous by-product of the reactions being  $\text{O}_2$  and  $(\text{P}_2\text{O}_5)_2$ . The release of oxygen will change the system oxygen partial pressure until the gas is removed from the vicinity of a phosphate compound, impacting reaction kinetics. In a refractory, this would mean the oxygen must diffuse

from the refractory by pore diffusion. As reported in the references, if the oxygen and phosphorous containing gases encounter alumina at a lower temperature, they may reform aluminum phosphate, accounting for the movement of phosphate compounds within a brick or a gasifier.

Because refractories containing phosphates are made or used in oxygen environments ranging from atmospheric to low oxygen partial pressures, this study targets evaluating aluminum phosphates over a range of temperatures (from room to 1550 °C) and at two oxygen partial pressures (atmospheric O<sub>2</sub> partial pressure = 10<sup>-0.68</sup> atm and an oxygen partial pressure = 10<sup>-10</sup> atm). Phase changes studied and reported in this paper are associated with two types of aluminum phosphates - aluminum metaphosphate [Al(PO<sub>3</sub>)<sub>3</sub>] and aluminum orthophosphate [AlPO<sub>4</sub>].

## 2. Equipment/Experimental Procedure, and Phosphate Materials

### 2.1 Analytical Equipment and Test Procedure

Thermodynamic calculations, the equipment, and (where appropriate) the test procedures used to treat samples were as follows:

- The thermodynamic software “FactSage” (version 7.3) was used to predict stable phases existing in aluminum phosphate samples when exposed to a synthetic air mixture (21 wt pct O<sub>2</sub>/79 wt pct N<sub>2</sub> = an oxygen partial pressure of 10<sup>-0.68</sup> atm) and an ultra high purity CO/CO<sub>2</sub> gas mixture that created an oxygen partial pressure of 10<sup>-10</sup> atm at 1550 °C. Calculations were done using FactPS and FToxid databases, with emphasis on phosphate phases and reaction products.
- Thermogravimetric analysis (TGA) of weight changes occurring in two phosphate materials [Al(PO<sub>3</sub>)<sub>3</sub> and AlPO<sub>4</sub>] were measured from room temperature to 1550 °C in an atmosphere of synthetic air and a CO/CO<sub>2</sub> gas ratio determined by the thermodynamic software FactSage to give an oxygen partial pressure of 10<sup>-10</sup> atm at 1550 °C. The TGA used was a Thermo Fisher Scientific Model Thermax 700 TGA. High purity N<sub>2</sub>, CO and CO<sub>2</sub> gases supplied by Matheson (USA) were used throughout the test, with flow controlled using mass flow meters set for a combined flow of 50 ml/min (10.5 ml/min O<sub>2</sub>, 39.5 ml/min N<sub>2</sub> for the synthetic air = 10<sup>-0.68</sup> O<sub>2</sub> pp; and 46.9 ml/min CO, 3.1 ml/min CO<sub>2</sub> for the 10<sup>-10</sup> O<sub>2</sub> pp). Starting sample weights of 50 mg were evaluated for each aluminum phosphate test, which was spread evenly at a thickness of approximately 0.4 mm over the bottom of a 99.8 wt pct Al<sub>2</sub>O<sub>3</sub> crucible. Samples were

heated at 3 °C/min to 1550 °C, then held at that temperature for 8 hrs.

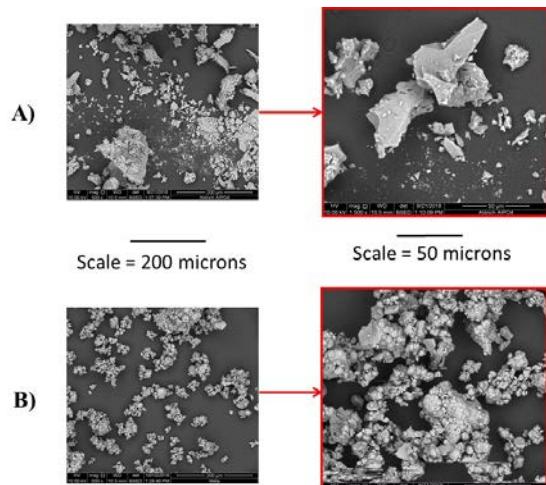
- Crystalline phases were identified by X-ray diffraction (XRD) analysis using a Rigaku Ultima IV XRD spectrometer (Cu K, 40 kV, 40 mA).
- Microstructure of powders was studied using a scanning electron microscopy (FEI) and energy dispersive X-ray (EDX) spectroscopy [Oxford INCA X-ray energy dispersive spectrometer].

### 2.2 Phosphate Material Properties

General physical properties of the two aluminum phosphate compounds evaluated in this research are given in **Table 2**, with SEM of the starting powders illustrated in **Fig. 1**. The chemistry of A is of an aluminum orthophosphate, and of B is an aluminum metaphosphate.

**Table 2 Characterization of the phosphate compounds evaluated in this study.**

Label	Mfg. Label Description	Room Temp. Phases (by XRD)
A	99.99 wt pct aluminum orthophosphate [AlPO <sub>4</sub> ]	100 wt pct amorphous
B	aluminum metaphosphate [Al(PO <sub>3</sub> ) <sub>3</sub> ]	100 wt pct Al(PO <sub>3</sub> ) <sub>3</sub>



**Fig. 1 Physical appearance of the two phosphate powders (A + B) listed in Table 1.**

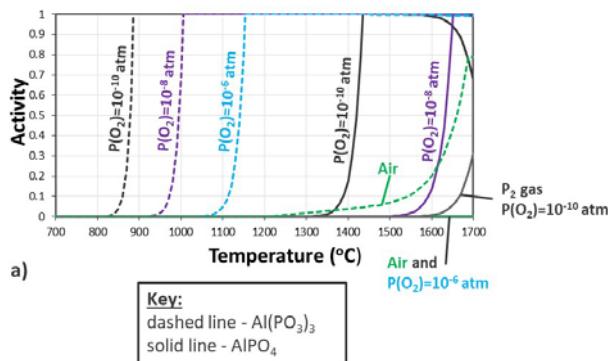
Note the “B” powder is much finer than the “A” powder, which appeared to be a mix of fractured individual particles vs the “B” powder, which appeared to be small and large agglomerates composed of smaller particles.

### 3.0 Results and Discussion

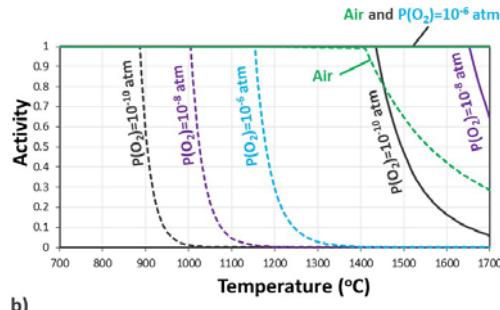
#### 3.1 Thermodynamic Studies

The thermodynamic stability of aluminum metaphosphate  $[\text{Al}(\text{PO}_3)_3]$  and orthophosphate  $[\text{AlPO}_4]$  at temperatures from room to 1700 °C, and at a range of oxygen partial pressures from atmospheric ( $10^{-0.68}$ ) to  $10^{-10}$  atm is shown in **Fig. 2**. **Fig. 2a** shows thermodynamic activity of produced P-bearing gases as a result of aluminum phosphate decomposition – a temperature and  $\text{O}_2$  pp dependent reaction. P-bearing gases are expected to form at lower temperatures with decreasing  $\text{O}_2$  pp in the system.  $(\text{P}_2\text{O}_5)_2$  was found to be a primary P-bearing gas phase at  $\text{O}_2$  pp =  $10^{-10}$ ,  $10^{-8}$ , and  $10^{-6}$  atm; while  $\text{P}_2\text{O}_5$  and  $\text{PO}_2$  are predicted along with  $(\text{P}_2\text{O}_5)_2$  in air. Note, at  $\text{O}_2$  pp =  $10^{-10}$  atm and above 1600 °C the presence of  $\text{P}_2$  gas is possible, when its activity started to rise. Aluminum metaphosphate is thermodynamically stable to higher temperatures with an increase in oxygen partial pressure (**Fig. 2b**), showing a breakdown in its structure above 1400 °C in air. The stable phase formed from  $\text{Al}(\text{PO}_3)_3$  breakdown is predicted by **Eq. 2** to be  $\text{AlPO}_4$ .  $\text{AlPO}_4$  is predicted to be thermodynamically stable (**Fig. 2b**) to about 1430 °C at  $\text{O}_2$  pp of  $10^{-10}$  atm, and again indicates increasing stability as the oxygen partial pressure increases. Note that aluminum orthophosphate is stable up to 1700 °C using FactSage's FactPS and FToxide databases.

Thermodynamic stability of P-bearing gases



Thermodynamic stability of aluminum phosphate

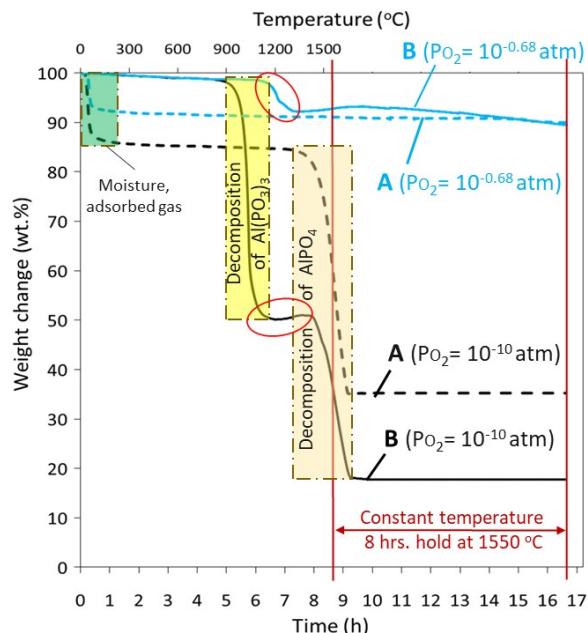


**Fig. 2 Thermodynamic stability of P-bearing gases and aluminum phosphate  $[\text{Al}(\text{PO}_3)_3]$ , and  $\text{AlPO}_4$  from 700-1700 °C and at oxygen partial pressures from  $10^{-10}$  to  $10^{-0.68}$  atm as predicted by**

FactSage. a) indicates the activity of P-bearing gases produced during the decomposition of the two phosphate compounds; and b) indicates the activity of the two aluminum phosphate compounds.

#### 3.2 Thermogravimetric Studies

Weight changes in 50 mg samples of A and B aluminum phosphate powders was measured in air ( $10^{-0.68}$  atm pp of  $\text{O}_2$ ) and at  $10^{-10}$  atm  $\text{O}_2$  pp. The results are plotted in **Fig. 3**.



**Fig. 3 TGA plot of weight changes occurring in aluminum phosphate compounds; orthophosphate (A =  $\text{AlPO}_4$ ) and metaphosphate [B =  $\text{Al}(\text{PO}_3)_3$ ] in air ( $\text{O}_2$  pp =  $10^{-0.68}$  atm), and at  $\text{O}_2$  pp of  $10^{-10}$  atm for a 50 ml/min combined gas flow of  $\text{O}_2/\text{N}_2$  or  $\text{CO}/\text{CO}_2$  as calculated at 1550 °C. Starting sample weight for testing was 50 mg. Red circled areas indicate unexplained weight changes.**

The weight loss in the low oxygen partial pressure environment ( $10^{-10}$  atm  $\text{O}_2$  pp) for the orthophosphate (A) in **Fig. 3** changed as predicted by FactSage in **Fig. 2b**, indicating a stable phase to higher temperatures with increasing oxygen partial pressure. It was noted in the air environment, the amount of weight loss at about 100 °C was about 50 wt pct less than measured at an oxygen partial pressure of  $10^{-10}$  atm. The cause for this difference is not known but is thought to be adsorbed moisture or gases. In contrast, the metaphosphate sample B showed no low temperature weight changes (around 100 °C) for either the air ( $10^{-0.68}$  atm) or  $10^{-10}$  atm partial pressure of  $\text{O}_2$ ; had a large weight loss between 900-1100 °C for  $10^{-10}$  atm  $\text{O}_2$

(corresponding to the  $\text{Al}(\text{PO}_3)_3 \rightarrow \text{AlPO}_4$  transformation as confirmed by XRD crystalline phase analysis); and had a large weight change between about 1100-1400 °C in both the  $10^{-0.68}$  and  $10^{-10}$  O<sub>2</sub> atm sample exposures (see **Fig. 3**, red circled areas). The weight change between 1100-1350 °C was not predicted by FactSage (**Fig. 2b**) and is being investigated. It is suspected that either the sample chemistry is not as indicated, a metastable phase exists, and/or that unknown reactions are occurring in the different gas environments. Note that the TGA curve for the B sample in the O<sub>2</sub> pp of  $10^{-0.68}$  atm had also indicated a long term weight increase, then decrease in weight starting at about 1350 °C through the 8 hr isothermal hold at 1550 °C. The cause of these changes is not known and is being investigated.

#### 4 Conclusions

The stability of two aluminum phosphate compounds [aluminum orthophosphate =  $\text{Al}(\text{PO}_3)_3$  and aluminum metaphosphate =  $\text{AlPO}_4$ ] were evaluated in a controlled environment TGA system from room temperature to 1550 °C in air and an oxygen partial pressure of  $10^{-10}$  atm, and were thermodynamically modeled in those oxygen partial pressures from room temperature to 1700 °C. The following phase changes were noted:

- 1) Increasing the O<sub>2</sub> partial pressure resulted in increased thermal stability of the phosphate materials as predicted by thermodynamics and as measured by TGA.
- 2) At a given O<sub>2</sub> partial pressure, thermodynamic modeling and TGA data agreed on major phase changes, and indicated aluminum metaphosphate decomposed at lower temperatures than aluminum orthophosphate.
- 3) For a given aluminum phosphate at given oxygen partial pressure, solid phase changes occurring with increased temperature will be as follows:  $\text{Al}(\text{PO}_3)_3 \rightarrow \text{AlPO}_4 \rightarrow \text{Al}_2\text{O}_3$
- 4) Unaccounted TGA weight losses occurred in AlPO<sub>4</sub> exposed to O<sub>2</sub> partial pressures of  $10^{-0.68}$  and  $10^{-10}$  atm at about 100 °C; in Al(PO<sub>3</sub>)<sub>3</sub> exposed to O<sub>2</sub> partial pressure of  $10^{-0.68}$  atm and  $10^{-10}$  atm between 1100-1400 °C as weight losses/gains; and in Al(PO<sub>3</sub>)<sub>3</sub> exposed to O<sub>2</sub> partial pressure of  $10^{-0.68}$  atm above 1350 °C as slight weight losses/gains ( $\pm 2$  wt pct). None of these changes were predicted by thermodynamic modeling. It is suspected impurities causing the anomalies existed in the starting aluminum phosphate materials, which is undergoing additional studies. The impurities may be a metastable phase, material chemistry, or unknown reactions.

#### References

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#### Disclaimer

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