

Hazards associated with the use of bone ash in contact with molten aluminum.

Don A. Doutre

Novelis Global Technology Center, Box 8400, 945 Princess Street, Kingston, Ontario, Canada, K7L 5L9

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Abstract

Bone ash (calcium hydroxyapatite or simply calcium phosphate) has traditionally been used in the casthouse to fill cracks, patch holes and cover “make and break” or moveable joints. It has many attractive attributes including its ease of use, low cost and non-wetting characteristics. Bone ash itself is non-toxic and environmentally benign. However recent evidence indicates that bone ash can be reduced upon contact with aluminum alloys to produce metal phosphides. Metal phosphides can in turn react with water or water vapor to liberate phosphine (PH₃) a highly dangerous and toxic gas. This paper reviews the observations and experiments that lead to this conclusion and discusses Novelis’ search to identify a satisfactory substitute.



Flow Control Pins

Indications that there might be issues relating to a reaction between bone ash and molten aluminum began with the arrival of a metal flow control pin that had been used in the casting of an aluminum 4.5% Mg alloy. Fused silica flow control pins were coated by dipping in an aqueous slurry of bone ash prior to drying and use. During casting, material would adhere to the sides of the pin in contact with the molten metal and on occasion the accumulation of material would choke off the metal flow leading to a cast abort. Figure 1 shows a flow control pin with an accumulation of material.

Introduction

For many years bone ash was widely used within Novelis casthouses. Applied as a dry powder, it was used to seal gaps and fill holes in metal transfer launders. As an aqueous slurry, bone ash was also used as a release agent and coating to protect tools, sow pans, casting pins and the like.

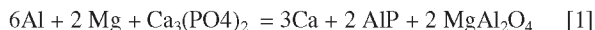
Over time a number of observations came together to suggest that bone ash was not fully inert when in direct contact with molten aluminum and that, under certain conditions, the products of the reaction could lead to the release of phosphine gas. This led to a search for a replacement material that would eliminate the possibility of producing phosphine.

The purpose of this presentation is to share these observations and concerns with the rest of the industry and to briefly describe the methodology used in our search for a suitable substitute.

Observations

PoDFA Samples

Bone ash is often reported in the analysis of PoDFA concentrates where it is generally associated with fine crystalline spinel particles. One proposed stoichiometry for this reaction being;



The AlP reacts with moisture during sample preparation and generally leaves a series of pits as the specimen degrades.

Similar behavior can be seen in samples taken from phosphorous modified hypereutectic silicon alloys where the volume change associated with the hydrolysis reaction [2] can cause the sample to visibly expand out of the mounting media.



Figure 1: Discoloration and accumulation of material on a bone ash coated flow control pin.

The area of the pin in contact with the metal had changed from pure white to a dark yellow/green brown. A very distinct garlic-like odor was released when the plastic bag containing the sample was opened and the odor became more intense when the sample came into contact with water during sample preparation. Due to the reactivity issue subsequent sample preparation was done using water-free fluids. Figure 2 shows and SEM image of the built-up material. EDX analysis indicated the presence of Mg, O and P along with only traces of Ca.

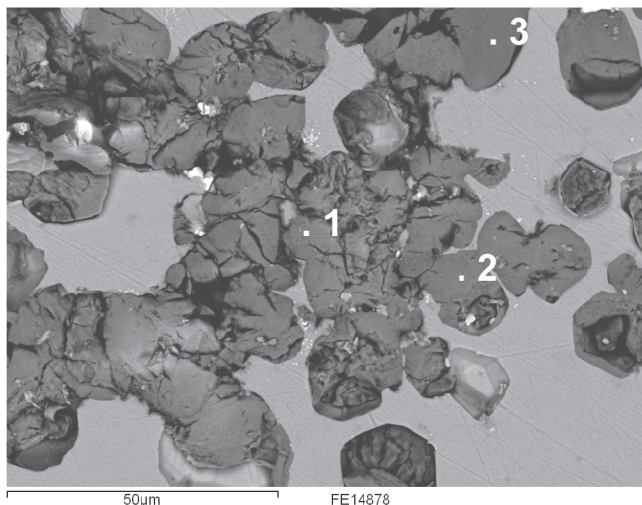


Figure 2: SEM image of a “dry-polished” section through the material adhering to the flow control pin.

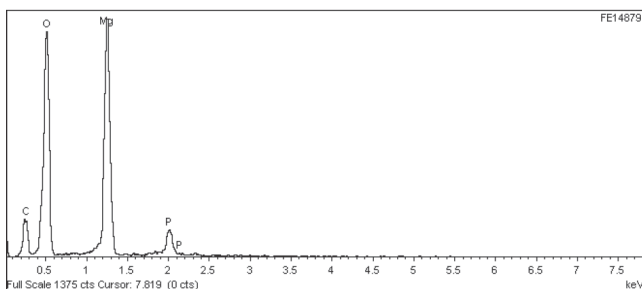
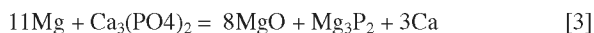
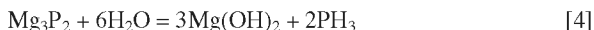


Figure 3: EDX spectrum of particles in Figure 2.

It would appear that, in high Mg alloys the reaction product is MgO, as opposed to MgAl₂O₄. These observations are consistent with the formation of a metal phosphide via the reaction:



Upon exposure to moisture the phosphide will hydrolyze to form phosphine gas. (In fact the phosphides of Mg, Al and Zn are widely used as fumigants for pest control in grain elevators.)



When the sample was intentionally moistened a very intense odor was released and the presence of phosphine was confirmed using both GC-MS and Draeger™ gas sensing tubes.

Metal Distribution Bags, Metal Transfer Launder, Dross Bins

Once it was realized that phosphine could arise as a result of the use of bone ash in contact with molten aluminum further sampling was carried out in and around the production centers. It was found that the fiberglass bags used for metal distribution within the ingot heads accumulate bone ash that becomes dislodged during casting. Later, as a result of their large exposed surface area, they can generate very high levels of phosphine gas when exposed to moisture in a closed environment. Levels as high as 800 ppm were found in sealed bags used to transport samples

back to the laboratory. Detectable levels of phosphine were later identified inside dross bins and storage areas and in the vicinity of transfer launders where the characteristic yellow/green/brown color associated with the reaction was readily observed (Figure 4).



Figure 4: Discoloration of base of transfer launder due to metal phosphide formation.

Salt Cake

A very surprising situation came to light when one of Novelis' dross tollers reported that the disposal of salt cake arising from the treatment of Novelis dross had been associated with landfill fires. The processor had taken great care to segregate drosses and to ensure that no “hot” salt cake residues were leaving their site.

Observations carried out at the dross toller revealed the following;

- 1- Salt cake from Novelis drosses would emit visible flames after brief exposure to water. The most reactive salt cake was associated with Mg-containing alloys.
- 2- The gas responsible for these flames could pass through water and ignite upon contact with the air. (Phosphine is insoluble in water and can ignite spontaneously upon contact with air)
- 3- The presence of phosphine was confirmed on site using Draeger™ tubes and later by GC-MS in wetted salt cake samples sent back to the laboratory.
- 4- The salt cake remained reactive when similar dross residues were processed by a different toller.
- 5- Drosses from other locations that were known not to be using bone ash did not emit flames or generate significant levels of phosphine.

Based upon these observations a test was conducted wherein bone ash was replaced with wollastonite (calcium silicate) on an alloy

and DC center previously known to be associated with the problem. Subsequent testing confirmed that the salt cake did not produce either flames or significant levels of phosphine upon exposure to moisture.

Identifying a Substitute for Bone Ash

Once the full potential for phosphine generation was appreciated, a decision was made to eliminate the use of bone ash throughout the Novelis system. Although the majority of the cast houses were using bone ash there were some using other materials including wollastonite and calcium carbonate. In addition a publication by Alcoa personnel indicated that they were using calcium carbonate [1].

The desired attributes in a substitute material would include,

- low tendency to absorb humidity
- chemical inertness
- lack of toxicity
- ease of use/compactibility
- availability and cost
- impact on metal cleanliness and remelting

A wide range of finely divided inorganic oxides are commercially available for a variety of applications including plastic fillers, paint pigments and extenders, paper whiteners etc. Based upon manufacturers' product data sheets, materials that appeared to have the potential to meet the criteria listed above were selected for further evaluation.

In order to rank materials in terms of their potential impact on metal cleanliness and reactivity when remelting, materials were exposed to and Al-5% Mg alloy at 700C and 900C. After exposure the melt was stirred and samples taken for chemical and inclusion analysis (OES and PoDFA). Table 1 shows a sample of the results obtained for some of the materials under consideration.

Table 1: Results of exposure tests (900C) of bone ash and potential substitutes

	Ca (ppm)	PoDFA (mm ² /kg)	Notes
Base alloy	1	n/a	
Bone Ash	128	9.1	P 4 to 33 ppm
Wollastonite	171	5.2	Si 0.05 to 0.18%
Mica Wash	9	17	Si 0.04 to 0.09%
Talk	6	22	Si 0.04 to 0.06%
Boron nitride	1	4.5	B 3ppm to 0.016%
TiO ₂	4	10	Ti 0.003 to 0.10%
kaolin	1	6	

The results indicate that all of the materials react with the alloy to some extent under the conditions of the test. In addition to a large increase in the calcium level, the metal exposed to bone ash gained 29 ppm of phosphorous. Even exposure to boron nitride, a substance generally regarded as inert to aluminum alloys, led to a substantial increase in the boron content of the metal. The fact that bone ash and wollastonite had been used successfully in this application for many years was used as a de facto standard against which the other materials were evaluated. Figure 3 shows an image of the PoDFA concentrate of metal exposed to wollastonite.

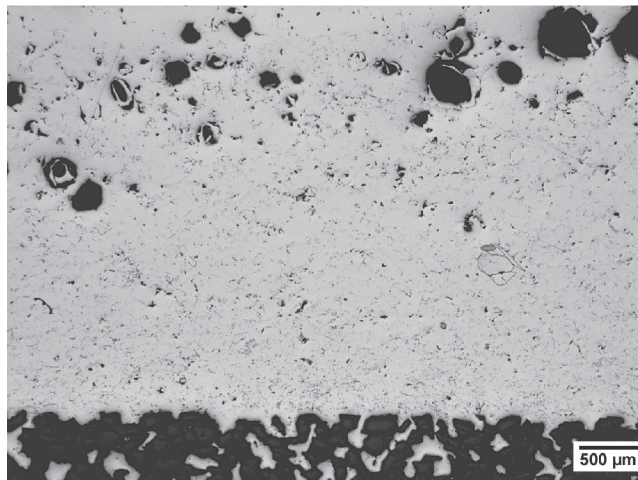


Figure 3: PoDFA concentrate of Wollastonite exposed to AlMg5

On this basis mica wash and talk were eliminated. Other materials were discarded based on cost and availability. Another factor used in determining suitability was the tendency for the materials to form clusters either by infiltration or reaction and clumping. An example of this behavior, seen in a PoDFA concentrate of a sample exposed to kaolin is shown in Figure 4. Clusters of inclusions of this size are of obvious concern in inclusion sensitive applications.

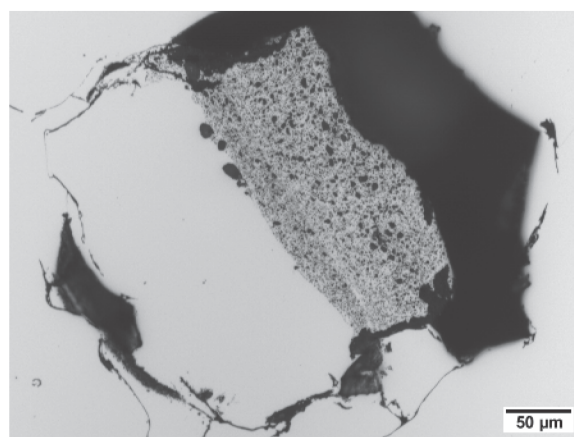


Figure 4: Infiltrated clump of reaction products seen in a PoDFA concentrate of metal exposed to kaolin powder.

Operator acceptance to the introduction of some of the substitute materials has been mixed. None of the substitute materials have the same ability to adhere or pack quite as well as bone ash. This has been very subjective and depending upon the characteristics of the local bulk mineral supplies, different locations adopted different materials as they phased out the use of bone ash. Since the elimination of bone ash there have been no further issues with landfill fires or phosphine.

Conclusions

Phosphine gas can be generated both within the casthouse and during dross processing as a consequence of the use of bone ash.

A two stage mechanism is responsible wherein metal phosphides are formed during the contact of molten Al alloys with bone ash to form metal phosphides which in turn react with moisture to liberate phosphine gas. During rotary salt processing these metal phosphides can become coated by a salt layer providing temporary protection. Upon exposure to rain or leachate in a landfill, the salts dissolve and phosphine gas can form, spontaneously ignite, and serve as the ignition source for landfill fires. A number of alternative materials were evaluated and put into service as replacements for bone ash in the casthouse.

Reference

1. D.D. Yancey and D.H. DeYoung, "Calcium Contamination of Molten Al-Mg Alloys by Calcium Carbonate", *Light Metals 1997*, TMS, pages 1035-1041.