

**DEVELOPMENT OF ALUMINUM DROSS-BASED MATERIAL
FOR ENGINEERING APPLICATIONS**

by

Chen Dai

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Approved:

Prof. Diran Apelian, *Advisor*

Prof. Tahar El-Korchi

Prof. Diana Lados

Prof. Makhlouf Makhlouf

Prof. Richard D. Sisson, Jr.

ABSTRACT

Aluminum dross is a by-product of Aluminum production. At present, dross is processed in rotary kilns to recover the Al, and the resultant salt cake is sent to landfills; although it is sealed to prevent from leaching, the potential for leaching exists and could harm the environment as the salt cake contains fluorides and other salts. Furthermore, much energy is consumed to recover the Al from the dross; this is energy that can be saved if the dross could be diverted and utilized as an engineering material. The objective of this work is to eliminate waste and instead utilize the waste in a natural cycle (closed loop) by using it as an engineered material. Three avenues were investigated to utilize the dross: (i) refractory materials; (ii) aluminum composites; (iii) high temperature additive for de-sulphurizing steel. We have found that the use of dross waste to manufacture refractory material has much merit. Mechanical property evaluations revealed the possibility for dross waste to be utilized as filler in concrete, resulting in a 40% higher flexural strength and a 15% higher compressive strength compared to pure cement. These results will be presented and discussed.

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1. INTRODUCTION

1.1 Definition of Dross and General Scope of Related Aluminum Recycling

Aluminum Dross is a by-product of Aluminum production. Today much energy is consumed to recover the Al from the dross; energy could be saved if the dross was diverted and utilized as an engineering material. There are two forms of dross – white dross and black dross. White dross is formed during the primary Al refining process, while black dross is formed during the secondary refining process, which uses relatively large amounts of Chloride salt fluxes. Subsequently, the dross is processed in rotary kilns to recover the Al, and the resultant salt cake is sent to landfills. Although salt cakes are sealed to prevent from leaching, the potential for leaks exists and in fact does occur which harms the environment. There is much merit if the dross that is formed could be “recycled” as an engineering product for specific applications. Interestingly the main constituents of dross are Al and Al_2O_3 , yet ironically, and MgO and $MgAl_2O_4$ as well, since there is much effort today to produce Al based composites containing a second phase constituents (such as Al_2O_3).

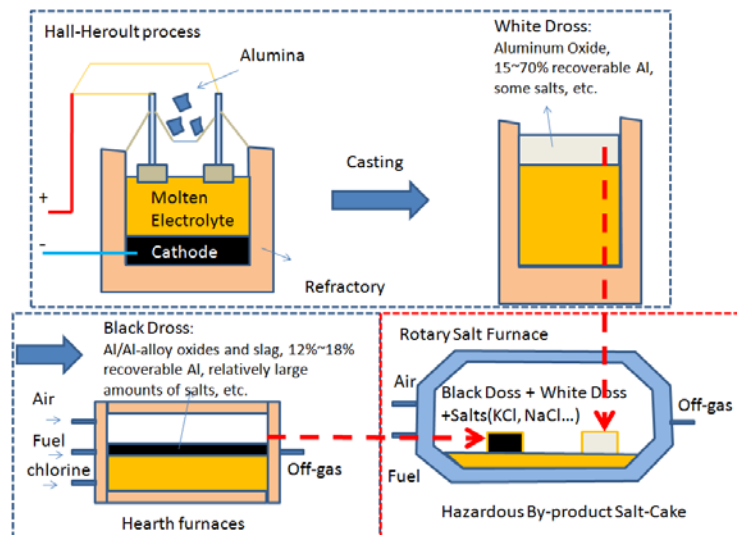


Figure 1: Schematic showing primary aluminum production and origins of dross.

Figure 1, above, shows the processing scheme and the processing of the dross by-product. It is interesting to analyze the scale of the issue. As seen in Figure 2, the traded new scrap is 1.6 million tons. This represents the weight of metal in skimming; however, the dross weight would be approximately 2 times of this amount, which is 3.2 million tons. To exacerbate the situation, recycled Al will produce more products, and this will result in a higher proportion of dross than from the use of primary Al; this is a considerable volume of metal and further emphasizes the need for channeling Al dross towards useful life for appropriate engineering applications. The mass flow chart, Figure 2, gives a good overview of the material flow for Al production. The metal loss of 1.7 million tons represents the data for 2008; no doubt this number will increase as consumption increases.

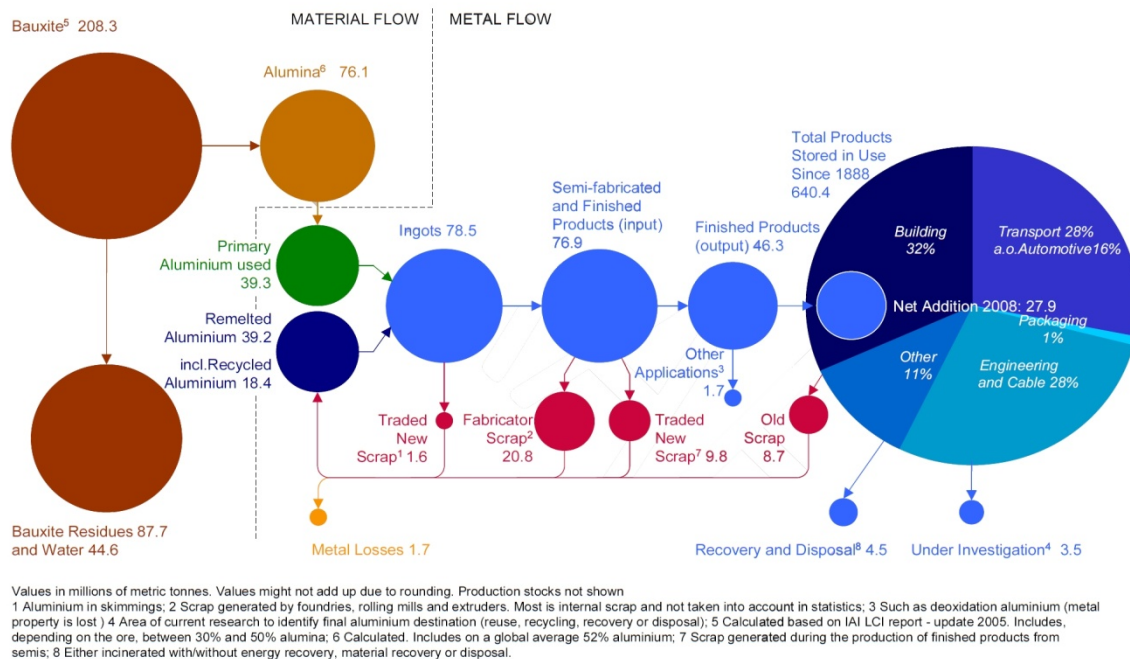


Figure 2: Mass flow paths in the production of aluminum [1].

The driving force to take an industrial waste such as Al dross and to use it as an engineering material is not only an issue environmental, but also an economic one. The impact of reducing energy consumption to recover the Al out of dross and to mitigate potential leakage from landfills is huge. In addition, the potential economic benefits are enticing.

1.2 Environmental Motives

In nature where we have an abundant set of examples of closed loop cycles, we find that nothing is “wasted”, as products in every step of the cycle have a utility for the next step in the cycle. So in a closed loop system, the earth survives millions of years, and that is what we call ecosystem. Unfortunately we cannot say the same for industrial system. In nature the target is equilibrium, whereas in our industrial system it is growth!

In 2008, the IAI (International Aluminum Institute) published a Sustainability Report [1] that gives targets (and goals) for the industry. Some of the key targets are:

- ⇒ A 33% (min.) reduction in fluoride emissions per ton of aluminum produced by 2010.
- ⇒ A 10% reduction in smelter electrical energy usage (per ton of aluminum produced) by 2010.
- ⇒ A 10% reduction in energy use (per ton of alumina produced) by 2020.
- ⇒ Aim at a global aluminum UBC recycling target of 75% by 2015.
- ⇒ Spent pot-lining has properties that make it a valuable material for the use in other processes.
- ⇒ Strive to convert all spent pot lining into feedstock for other industries or to re-use.

All above are leading to the necessity for us to take the production of dross seriously. This project, which aims to develop engineering applications for dross material, is in line with and has fidelity with the above goals. The economic impact for “recycling” aluminum dross is significant as it mitigates metal losses, alleviates the use of salts, and eliminates the need to landfill salt cakes.

1.3 Economic Motives

Recycling aluminum uses about 5% of the energy required to produce aluminum from bauxite, because the latter requires much electrical energy to electrolyze aluminum oxide into aluminum. Recycling results in significant cost savings over the production of primary new aluminum even when the cost of collection, separation and recycling are taken into account. Small percentage losses result in large losses, thus the flow of material is well monitored and accounted for financial accountability. It is understandable that metallic aluminum content in dross is of interest, as aluminum recovered has value to the enterprise.

When reviewing primary aluminum production, it can be noted that mitigating dross formation is the most direct means of making an impact to the bottom line. Degassing has been used, but this can only reduce 5% of dross and there is a cost associated with this step [2].

The other possibility is to convert dross recovery into a non-salt processing step. Recycling of aluminum dross without salt fluxes and using plasma torches has been developed in France, however it is more cost-effective. It is estimated that the investment for a production unit would be 20 million dollars per year, which mean 661 dollars will be added to the cost of dross for each ton produced [3].

The objective to use dross as an engineered product or as a component in engineered product system is a logical target. First, aluminum oxides from dross recycling comprise an alternative source to many primary materials. Second, if dross can be channeled towards a useful product, aluminum smelters can benefit by charging a gate fee for handing and processing waste dross.

2. BACKGROUND

2.1 Dross Formation

The products generated from aluminum melting furnaces fall in to three categories: (i) molten aluminum, (ii) off-gases i.e., CO₂, SO₂ and fluorides, and (iii) semi-solid mixture or aluminum dross.

It has been suggested that the chemical oxidation and physical entrapment during dross formation may contribute up to 50% of the total metal loss of ~1% in a typical primary aluminum smelter (i.e. 2,500 tonne/annum (tpa) in a smelter of 500,000tpa output)[4]. This is a large financial loss, and it also represents a significant carbon footprint. As a whole, the aluminum industry produces approximately 3.2 million tons of dross annually from domestic aluminum smelting.

Most of the interest has been on the recovery of the aluminum content of the dross, as white dross can reach as high as 80wt%. In order to recover the metallic aluminum, dross is heating in a rotating furnace with a salt flux introduced. This can help separate the molten aluminum from solid oxides and protect aluminum against oxidation. But when the aluminum is taken away, the rest of the dross along with the added salts (called salt cakes) is sent to landfills. Although they are sealed from leaching, the potential of leaching exists and soluble salts represent a serious source of pollution to both soil and surface/underground water supplies.

2.2 Characterization of Aluminum Dross

2.2.1 Dross classification

Dross can be divided into 2 types, (i) non-salt containing or white dross; (ii) salt containing or black dross [5, 6, 7, and 8].

Typically, white dross is produced when melting using salt flux. It has a high metal content and is compacted in large clotted lumps or blocks. It consists almost entirely of Al₂O₃ and aluminum metal trapped by the surface tension of the oxide skin. In contrast, black dross is granular with a high metal content in coarse fraction and chiefly oxides and salts in the fines.

2.2.2 Physical and chemical properties

Mafриди, Wuth and Bohlinger in Berlin have carried out a complete analysis of physical and chemical properties of dross [9]. They evaluated six granular and five compact dross samples from different smelters and foundries. The bulk density of granular dross was determined according to DIN 52110-B, while DIN52102-RE-VA was applied to compact dross [10]. The salt contents of the dross were measured by applying the leaching test DIN 38414-S4; the metal contents by the salt-melting process were measured on a laboratory scale. Also a 100g sample was mixed with distilled water and stirred in a closed vessel to measure gas evaluation. The results are shown in Table 1.

Table 1: Range of physical and chemical properties.

Properties	Granular Dross	Compact Dross
Alloy Content (%)		
Melt	2.44–11.77	1.34–10.03
Recovered Metal	1.03–5.51	0.33–6.80
Distribution(q) (mm ⁻¹)	0.08 (coarse)–0.452 (fine)	—
Density (t/m ³)	0.828–1.118 (bulk)	2.396–2.528 (apparent)
Metal Content (%)	46.9–69.1	71–93
Lixivate (pH)	9.52–10.14	9.03–9.48
Salt Content (%)	0.18–6.21	0.01–0.03
Gas Evolution (l/kg dross)	0.25–1.17	No evolution

2.2.3 Chemical composition

Generally, dross is made of aluminum oxides, remaining metallic aluminum, nitride, carbide and sulfide of aluminum, and salts and some alloying elements.

Yoshimura and Abreu [11] evaluated the composition of raw aluminum dross waste by semi-quantitative X-ray diffraction analysis. In order to evaluate the equivalent oxide content of metallic elements, the waste was calcined at 1450°C for an hour in air. Calcination resulted in oxidation of phases such as AlN, metallic Al and CaF₂, and the remains consisted mainly of corundum and spinel phases, with small amounts of β-Al₂O₃ (Table 2).

Table 2: Composition comparisons of raw dross and calcined dross (wt%).

Raw Dross		Calcined Dross	
MgAl ₂ O ₄	48	Al ₂ O ₃	84
AlN	28	MgO	11
α-Al ₂ O ₃	7	SiO ₂	2
(NO) ₂ Al ₂₂ O ₃₄	6	CaO	1
NaAl ₁₁ O ₁₇	6	Na ₂ O	0.7
CaF ₂	3	K ₂ O	0.4
Al	2	Fe ₂ O ₃	0.3
		TiO ₂	0.3

The chemical composition of aluminum dross particles before and after a purification procedure (boiling water with stirring, cool water, milling, and vacuum filtration) is compared by Kevorkijan [12]. After purification the main constituent in the final product is aluminum oxide. The aluminum hydrolyzed during the heat treatment in water to Al₂O₃. The results are given in Table 3.

Table 3: Composition comparisons of dross (as-received) and after purification.

	As-received (wt%)	After purification (wt%)
Al ₂ O ₃	78.24	94.74
SiO ₂	1.46	1.56
Na ₂ O	6.28	0.03
CaO	0.47	0.03
TiO ₂	0.13	0.13
MgO	1.97	0.03
K ₂ O	1.47	0.03
Zn	0.05	0.53
Cu	0.51	0.55
Mn	0.03	0.03
Fe	1.00	1.07
Al _{metallic}	1.16	1.24
AlN	7.23	0.03

2.3 Recovery Process

2.3.1 Proposed concepts

Several technologies have been proposed to address the potential hazards of salt cakes in landfills. Some of them involve water leaching of salts from salt cake at high temperatures and pressure (Bodnar et al., 1997) [13], the use of plasma arc and low oxygen furnaces (Schirk, 1997)[14] or even eletrodialysis for the recovery of salts from leaching solutions (Sreenivasarao et al., 1997)[15]. These alternative techniques are not economically feasible, and do not maximize aluminum recovery; they also produce aluminum oxide and other residues, which require landfill disposal.

2.3.2 Patented methods

Over the years several concepts have been proposed. Papafingos and Lance's work in 1978 [16], befits Einstein statement: Everything should be made as simple as possible, but not simpler. The patent features equipment for cooling and disaggregating aluminum dross with water in order to dissolve the salts. During the digestion step, several undesirable and potentially toxic chemical reactions end up producing hydrogen, methane and ammonia gases. This procedure cannot remove all the undesirable ingredients effectively, but it does remove most.

Yershalmi introduced PH control in the digester to prevent undesirable reactions [17]. In this method, the pH is maintained in the range of 5 to 8 by adding magnesium chloride, which can be taken from a crystallizer that recovers the salts from the process. Accordingly, non-dissociated Mg(OH)₂ and HCl are formed, and the latter can decrease the pH and consequently slows down the AlN's and Al's reactions with water. Although it is only a way of suppressing, this method recycles Mg from aluminum dross without increasing the overall amount of MgCl₂ in the system.

Pickens and Waite discovered an interesting method for the valuable products from dross solution to precipitate gradually by controlling the PH [18]. At the very beginning the undissolved magnesium aluminate is separated by filtration. When the pH is raised to about 9.5-12, magnesium oxide appears and is soon to be removed by a filter. With a pH of about 10-11,

the aluminum is held in solution and the mixed oxides remains as solids that are also removed by filtration. When the pH of the remaining liquid nears neutrality, aluminum rehydrate precipitates and the result is a substantially pure product.

Besides the above methods using water, there is another widely applied way to treat dross produced by the melting process of used beverage cans [19]. It aims to recover some valuable salts with a mixture of sodium borate-sodium chloride as salt flux as described in the previous paragraphs. Therefore, new dross is generated (black dross and salt cake).

2.4 Potential Applications

There is much merit if the dross could be “recycled” as an engineering product for specific applications. On one hand, dross is considered as a hazardous waste, on the other hand as a rich source of alumina. After much analysis, three application families have been identified: (i) use dross in refractories, (ii) use it in composites, and (iii) in slag modification. These are briefly reviewed below.

2.4.1 Refractory material

Alumina is the primary ingredient for a significant portion of the refractory products used in high-temperature industrial applications; such as metallurgical, cement, ceramic, glass, and petrochemical manufacturing processes [20]. World consumptions of calcined refractory-grade bauxite are about 1 million tons per year and calcined alumina for use in refractory applications is about 500,000 metric tons per year [21]. Thus there is some market potential for Al dross waste as an alternative alumina source for refractory aggregates.

Dunster [22] has shown that white/black dross can be used in concrete and asphalt products as filler (<700 μm .). As filler in asphalt, dross may improve stiffness, abrasion resistance and control micro-cracking. Yoshimura has shown that Al dross waste from plasma processing can be applied directly, without prior calcinations, as a fine structural component in castables and pressed refractory material [14].

The potential benefit of channeling aluminum dross towards refractory material is obvious. First, Dross is a great source of aluminum oxides, thus, it is an alternative source to primary materials. Second, aluminum smelters benefit by charging a gate fee for handling processing waste dross, and increasing the value of the end product of aluminum recycling process. Of course, it also reduces the waste disposed to landfills.

On the other hand, the potential barriers cannot be ignored. Both white and black dross may include undesirable compounds such as chlorides, fluorides, heavy metals and metal aluminum, which could adversely influence the composition of feedstock for cement manufacture. It is common practices to include blending and classification for cement kiln constitutes to minimize the impact of such contaminates.

2.4.2 Al-Alumina composites

After many years of research, discontinuously reinforced metal-matrix composites (DRMMCs) are moving from the research laboratory into industrial use. Inspection of the tensile properties of these different composite materials shows that a slight improvement in strength over the unreinforced matrix is achievable by the introduction of fine dross particles with a particle size less than 10 μm . Whereas, in composites with larger dross particles such strengthening effect

was not observed. By contrast, evaluation of the wear properties indicates that the introduction of coarse and even as-received dross particles into an aluminum matrix results in a significant improvement in the wear resistance of the composite material [23].

The DRMMCs can be achieved in two ways. One was prepared by a conventional rheocasting technique. The equipment used in this work is illustrated in Figure 3.

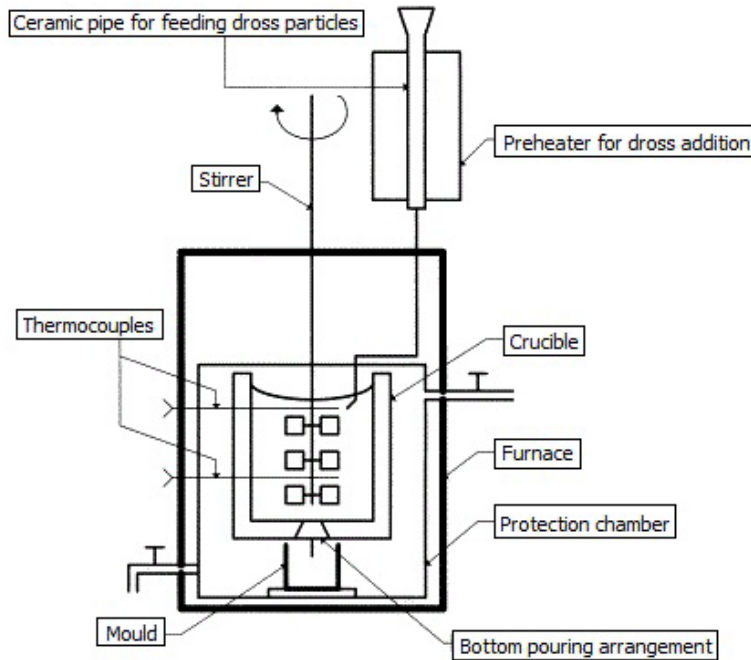


Figure 3: Experimental Equipment for Rheocasting.

Approximately 2 kg of the A356 alloy was melted in the crucible for each experiment and then heated to 10 K above its liquidus temperature. In parallel, the aluminum dross particles were preheated to 723 K for 1 h before being added to the crucible. As the melt reached the operating temperature, the preheated aluminum dross particles were added near the top of the mushy alloy using the refractory baffle and argon as a carrier gas. The baffle was immersed 5 mm below the surface of the mushy alloy with a tilt angle of about 45° in the direction of flow. The average feeding rate was 0.2–0.6 kg per hour. Once the aluminum dross particles were completely added, isothermal agitation of the melt was maintained for 20 min to obtain a uniform distribution of the reinforcement through the matrix.

Friction Stir Processing (FSP) is another means of incorporating dross in a matrix to manufacture localized composites. As a recent outgrowth of the Friction Stir Welding (FSW) process, FSP has been shown to eliminate casting defects and refine the microstructure at pre-determined location; this results in improved mechanical properties and enhanced corrosion resistance. There is a growing need for Al metal matrix composites, and FSP is a viable means of producing components with localized composite structure. How does the process work? A high-speed rotating tool with a flat shoulder and probe penetrates into the pre-fixed work piece; once full contact has been made between the head face of the tool shoulder and the work piece, the non-

consumable tool traverse across the work piece. Frictional heating (between the tool and the work piece) is high enough to ensure the needed plastic deformation of the matrix around the moving tool. The second phase is emplaced within the work piece and is transferred within the matrix, and finally it is dispersed in the FSP processed zone area. Producing metal matrix composites using FSP has advantages compared to traditional manufacturing methods: (i) the composite layer is fabricated locally at pre-determined zones rather than throughout the whole bulk; (ii) FSP processing can easily be carried out as a post casting operation, such as during the machining stage; (iii) since FSP occurs in the solid state, hydrogen porosity, residual stress, as well as many unwanted interfacial reactions between the reinforcement phase and the matrix are mitigated.

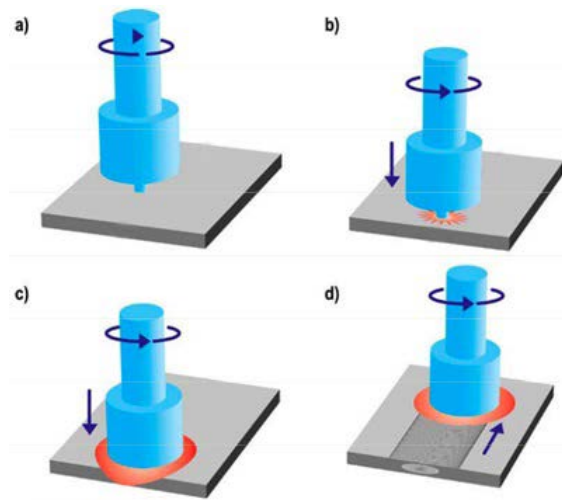


Figure 4: Friction Stir Processing (FSP).

If DRMMCs are to have any realistic application in the automotive industry, the engineering properties that make them valuable must be available at a competitive cost compared to their unreinforced counterparts. In other words, in DRMMCs for automotive application a competitive quality–cost relationship has to be established, taking into account that the material will be utilized only if the additional cost of the composite is justified by the improved performance.

2.4.3 Slag modification

Modification of the steel slag by Al dross essentially utilizes the calcium aluminates as a protective cover for the molten steel.

The possibility of producing calcium aluminates by fusion of lime (CaO) and alumina (Al₂O₃) is well known and documented [24]. Gens (1992) disclosed a process for heating aluminum dross and lime at temperatures in excess of the dross slag melting point of approximately 1400°C to produce two main products, aluminum metal and calcium aluminates.

Breaultn (1995) improved the method and obtained the composite by maintaining a calcining temperature of 1200°C or higher for 5 minutes, which is sufficient to form a friable sintered product rich in calcium aluminates [25]. Optionally, calcium fluoride or other fluoride can be added to the starting mixture, if it is not already contained in the dross residue.

In addition to thermochemical methods, classic chemical methods can also be used. For example, Morozova proposed the dissolution of calcium carbonate in an aqueous solution of aluminum chloride followed by a reaction with ammonium hydroxide to produce mixed Al-Ca hydroxides, which are subsequently dried and calcined to form calcium aluminates [26].

Schornikov, Stolyarova and Shultz [27] present another approach. They describe the preparation of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ by a precursor method, which consists in dissolving metallic aluminum and calcium carbonate in diluted nitric acid and reacting the aluminum-calcium nitrates with tartaric acid, heating the resulting mixture, evaporating the liquids, and calcining the remaining solid to yield calcium aluminates.

3. OBJECTIVES

Aluminum Dross is a by-product of Aluminum production. At present, dross is processed in rotary kilns to recover the Al, and the resultant salt cake is sent to landfills; although it is sealed to prevent from leaching, the potential for leaching exists and harms the environment as the salt cake contains Fluorides and other salts. Furthermore, much energy is consumed to recover the Al from the dross; this is energy that can be saved if the dross could be diverted and utilized as an engineering material. So the objective of the project is to eliminate ineffectively “refurbishing the waste“, and instead utilize the waste in a natural cycle (closed loop) by using it as an engineered material. Specifically, three paths were investigated:

1. Use dross to make refractory materials such as brick, or used in concrete as filler. We have found that dross particles can be mixed well with cement. This improves stiffness, abrasion resistance, and controlling micro-cracking of the material.
2. Use dross to make Al composites. We have found that dross powders are well dispersed in aluminum alloy matrix via friction stir processing; the product provides superior wear resistance with some sacrifice in strength. This certainly is a viable use of Al dross.
3. Use dross as a high temperature additive for de-sulphurizing steel slag. The dross can be used as an additive to the slag to modify the chemistry. However, for this application, only primary dross can be considered, because we need to alleviate fluorides in the dross.

Accordingly, for each path, the objectives of the research program are threefold:

- ⇒ Analyze the dross as produced in the Al production cycle
 - Composition, microstructure, morphological analyses of constituents, etc.
- ⇒ Analyze market needs for dross-like concrete/composites/chemistry for appropriate engineering applications
 - Literature review and market analyses through ACRC consortia and MPI members
- ⇒ Process the dross for useful engineering applications. Evaluate and characterize the processed dross in the laboratory and also validate with beta-site partners.

4. EXPERIMENTAL

4.1 Basic Properties

Two types of dross sample sent from different smelters and foundries in ALCOA were examined. One of them was from primary smelter – this dross would be mostly un-alloyed and would come contaminated with cryolite (Type I). And the other was produced in the casthouse – this would be mostly alloyed (Type II). They were screened and milled at Colorado School of Mines (CSM). A flow-chart is given below (Figure 5) describing where the samples were obtained.

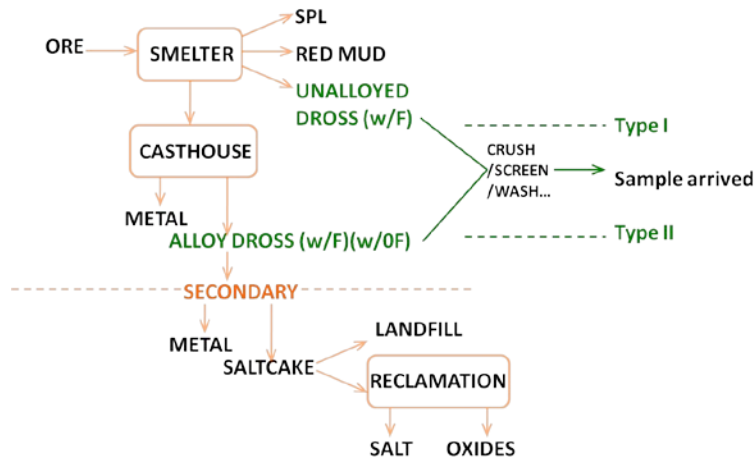


Figure 5: Flow of metal in a typical smelter-casthouse-secondary arrangement.

4.1.1 Morphology

Samples came to our lab sealed in white barrels as hazardous waste. Both Type I and Type II dross samples appear as mixtures of granular and compact dross. The focus is on the fine fraction of dross samples, so samples are crushed by hammer to obtain a finer appearance. It is worth mentioning that Type I dross is in a very loose structure that can be easily crushed by hand.

4.1.2 Size distribution

CSM has milled those dross samples to three grades; they are +3/4'', -3/4''~+1/4'' and -1/4''. Later, the finest portion is sieved to +600 μ m, -600 μ m~+300 μ m, -300 μ m~+150 μ m and -150 μ m. Then all these fractions are weighed for a better understanding of the particle size distribution.

4.1.3 Density

Samples of granular dross are put into a vessel of known volume to measure for bulk density. Samples of compact dross are taken by removing small pieces from different parts of big blocks. The apparent density is obtained by measuring their weight in air and the volume of the pieces in liquid. Afterward, the dross is melted to see the fusibility.

4.1.4 Leaching test

The leaching test is carried out by mixing a 100g sample with one liter of distilled water for 24 hours in an open vessel to determine PH value of the solution and see if there is any bubble (gas releasing reaction) coming up during the process.

4.1.5 Microstructure

Larger particles (>1cm) are mounted into small cylinders to view through optical microscope. And the finer portion, which appears as powder material, is placed on conductive tapes for scanning electron microscope (SEM).

4.1.6 Microhardness

Because the pieces of dross are complex mixture of all kinds of impurities in granular structure, small pieces tend to fall off the samples from time to time. At this point, they can hardly be tested in their original shapes. Thus, making dross particles dispersed in Al alloy matrix to form a composite becomes a reasonable solution to this problem. Consequently, friction stir processing (FSP) technique is applied here and dross powders are hold by aluminum alloy matrix, which, in this case, is A206. The next step is using diamond probe to punch wherever wanted under the microscope for the hardness testing.

4.1.7 Chemical composition

Powdered dross in different size grades are collected and examined through X-ray diffraction (XRD) tester for compounds and phases. SEM tests in 4.1.4 are also followed by Energy-dispersive X-ray spectroscopy (EDS) for element constitution information.

4.2 Purification/Preparation of Dross

Powder dross samples are processed with boiling water and the liquid mixtures are placed steady to let stratified. They usually divide into three clearly separated parts: the first one covers over the solution and floats on the liquid (foam), the second one sits down in the bottom but as an upper layer, the last one sinks in the real bottom. The XRD and EDS results show that the last two layers have relatively simpler compositions and the floating foam contains all of the complex ingredients. Therefore, it seems to be a feasible way to separate different components in dross material. A simple but effective conditioning procedure was designed:

- i. Take a 100g sample, mix with 1 liter distilled water, and stir the mixture in an open beaker.
- ii. Turn on the magnetic heating plate placed under the beaker and keep boiling for 1 hour. Cool down beaker in air and place it under the hood for 24 hours to let contaminations react completely.
- iii. Scoop out the floating foam and separate the insoluble remainder from the solution by filter.
- iv. Dry the insoluble portion in a crucible under $\sim 400^{\circ}$ F for 1 hour.

The powder material left in the crucible is what is needed and will be applied on all particle sizes ($-600\mu\text{m} \sim +300\mu\text{m}$, $-300\mu\text{m} \sim +150\mu\text{m}$ and $-150\mu\text{m}$) in all following experiments. Samples that have been through this procedure will be marked as received and washed (ARW) from this point.

4.3. Refractory Material (Concrete)

The main concept of this concrete experiment is to characterize the dross as a product in industry cycle and see if it can be added to cement mixture to form a dense and durable body.

4.3.1 Groups

Four groups of dross samples are arranged with different types of dross and different preparation procedures: Type I (as received- AR) and Type I (as received and washed - ARW); Type II (as received - AR), and Type II (as received and washed - ARW). All four groups were mixed with

Portland cement powder in different ratios. The matrix shown in Table 4 provides the arrangement used for all groups.

Table 4: Experimental matrix used for concrete part.

Samples							
AR				ARW			
Type I		Type II		Type I		Type II	
<150 um	20%	<150 um	20%	<150 um	20%	<150 um	20%
	10%		10%		10%		10%
150-300 um	20%	150-300 um	20%	150-300 um	20%	150-300 um	20%
	10%		10%		10%		10%
300-600 um	20%	300-600 um	20%	300-600 um	20%	300-600 um	20%
	10%		10%		10%		10%

Also, two kinds of control groups (CG) were designed for data comparisons:

- CG₀: 100% cement
- CG_i: cement and fine sand

Besides the pure Portland cement group (CG₀), which serves as a control group for all comparisons, each group listed above has its own specific control group (CG_i) with dross powder replaced by fine sand in the same particle size. For example, one group of 90% cement powder and 10% dross powder in 150µm is compared to a specific control group CG_i that is made of 90% cement powder and 10% fine sand in 150µm.

In all groups, cement refers to Type I Portland cement; it is general-purpose cement suitable for all uses where the special properties of other types are not required. Its uses in concrete include pavements, floors, reinforced concrete buildings, bridges, tanks, pipes...

4.3.2 Molds

For concrete, the most important properties must be compressive strength and flexural strength. Compressive strength is the primary physical property and frequently used in design calculations for bridges, buildings and other structures. And the flexural strength is used to design pavements and other slabs on ground. Considering the limited amount of dross we had and all groups of experiments we were planning to do, I decided to build molds by myself for testing these two properties. As shown in the Figure 6 and Figure 7, we designed and machined removable stainless steel molds for beams (4''x1''x.5'') and gashed polyvinyl chloride (PVC) tubes for cylinders (D=1.5'', L=4.5''). They were used for 3 points flexural strength testing and compressive strength testing accordingly. You may notice that we've deviated from American standard testing, thus, we have to keep the size consistent for all groups.

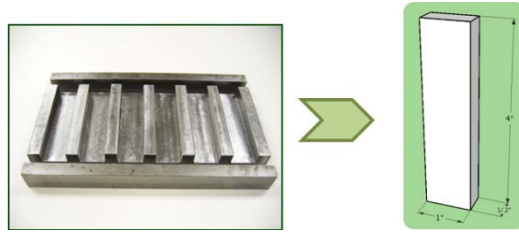


Figure 6: Molds for beam samples designed for 3-points flexural test.

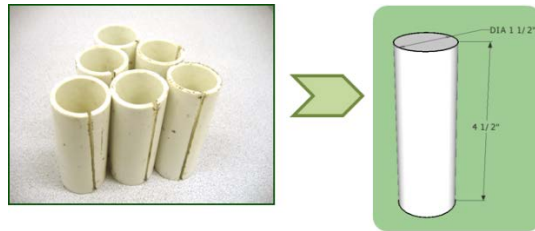


Figure 7: Molds for cylinder samples designed for compressive test.

4.3.3 Experimental steps

Using the 10% dross case as an example, the following sequential steps describe the experiment followed. Tests using other fractions should follow similar steps:

- i. Weigh 100g dross powder and 900g Portland cement powder and mix them in the blender bowl.
- ii. Pour 400g water into the bowl and turn on the blender to medium speed.
- iii. Blend for about 2 minutes to get a homogenous paste.
- iv. Scoop the paste out, fill both molds as quickly as possible and flatten the surface.
- v. Place them in the curing room with 100% moisture for one day.
- vi. De-mold the beams or cylinders, and place them back in the curing room.
- vii. Take them out at the 7th day and the 28th day for testing.

Notice that the amount of material described above is suitable for 6 beams and 3 cylinders. And the water-cement ratio must be kept as a constant (40%) during all the experiments.

4.3.4 Tests

Basically, we need to determine whether a dense body can be formed. We define the feasibility as shown in Figure 8. The ones that expand much in the mold with an unaccepted up lifting surface and a loose structure are considered to be an unsuccessful case. The successful cases are the ones that have flat surfaces and dense structures. Precisely, the ingredients are not apt to segregate during blending and the beam becomes homogenous mixture of all the components during concrete hardening.



Figure 8: Typical comparison for failed case (left) and successful case (right).

Next, for those who are considered to be successful cases, following tests are applied.

4.3.4.1 Density

Beams and cylinders are measured for weight and volume to calculate the apparent density.

4.3.4.2 Flexural strength and compressive strength

For each case, 6 beams and 3 cylinders are tested for flexural strength and compressive strength, respectively. Fatigue loads are recorded at the peak value of the strain-stress curve. Then the load is converted to stress in consideration of dimension changes for three point flexural tests:

$$\sigma = \frac{3FL}{2bd}$$

- F is the load (force) at the fracture point
- L is the length of the support span, L=3.8 inches
- b is width, b=1 inch
- d is thickness, and d varies from sample to sample regarding how much gas produces inside

Compressive testes also need similar conversion:

$$\sigma = \frac{F}{A}$$

Where, F = load applied, A = area

4.3.4.3 Microstructure

Porosity is essential to determine a concrete material's properties and people often use water absorption tests or pressure air measurements [28] to characterize porosity of concrete material. To get more intuitive results rather than a single porosity value, however, two measurements were applied to reveal the voids' sizes, fractions, and distributions: apparent density and optical microstructure. At this point, a 3D optical microscope is introduced into the testing part to achieve a closer look at the fatigue surfaces.

4.4 Aluminum Composites

Preliminary work for Al-composites is also realized here. It is said that aluminum alloy with fine dross particles dispersed in it produces superior wear resistance with some sacrifice in strength. Two ways are tried to obtain the composites. The first one is using FSP technique, namely friction stir processing. A cylindrical-shouldered tool is applied to the work piece. It is rotating at a constant speed and fed at a constant traverse rate into the plate material. Dross powder is placed in a thin groove on it, and the tool is made stir along the groove. In this way, dross powder is blended into the alloy matrix. The other way is casting. That is to add dross powder in liquid state aluminum via stirring, which includes manual stirring and degassing stirring. Note that, in this part, only Type II dross is used.

4.4.1 FSP

The friction stir processing is applied to our dross particles using A206 as the matrix. Sometimes, it is necessary to let the cylindrical tool go over the groove several times to achieve a better dispersion. After this, the composite samples are placed under the optical microscope to test for particle hardness and SEM is used to verify the dispersed phases and particle composition.

4.4.2 Casting

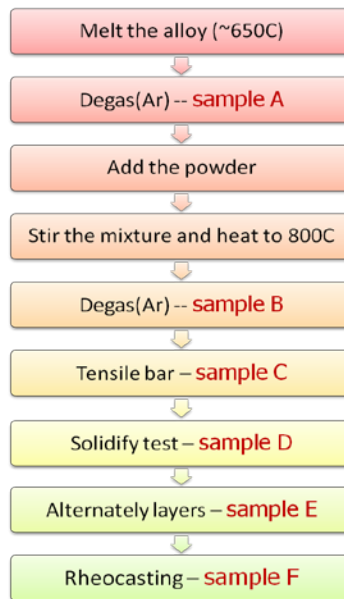


Figure 9: Steps of a typical casting experiment.

The figure above illustrates the experimental steps and the locations of all the samples in the flow chart. Sample A is made for OES testing for its original composition and Sample B is made for composition after dross powder being added. Sample C will be tested for tensile strength later.

A new consideration presented itself when working with this set of experiments. Exothermic topping extends the time required for liquid metal to get solidified. So Sample D is formed under the cover of fine dross particles to see if dross powder can be used as an exothermic topping in casting, because of its heat generation and retention properties. These properties result from its high content of metallic aluminum fines as well as aluminum oxide.

Sample E and Sample F are designed for a better dispersed region. The former one is obtained by pouring liquid metal and dross powder in a cylindrical mold alternatively, while the latter one is gained by stirring dross powder into liquid metal to form a marsh zoom. All samples above are cut and mounted to fit into the SEM machine.

5. RESULTS AND DISSCUSION

5.1 Basic Properties

5.1.1 Morphology

Both two kinds of samples came to me were sealed in white plastic barrels (50lb). An ammonia-like smell can be noticed as soon as the cover is removed. There are about 30 pieces of dross placed in it and each of them is as big as an adult's fist. Also the caps among all the compact pieces are filled with granular (sand-like) fraction.

Type I dross shows a relatively loose structure and can be crushed by hammer into very fine powder, while Type II dross appears to be very rigid. Neither hammer nor saw can break the compact pieces. At last, large blocks of Type II are broken into small pieces by dipping into liquid nitrogen and hot water alternatively using expansion and contraction mechanism.

5.1.2 Size distribution

After screening, milling, and sieving, size distribution of Type I dross is shown below. The finest particle (<150µm) constitutes about 30% (calculated by 70%*42%) among all the grades.

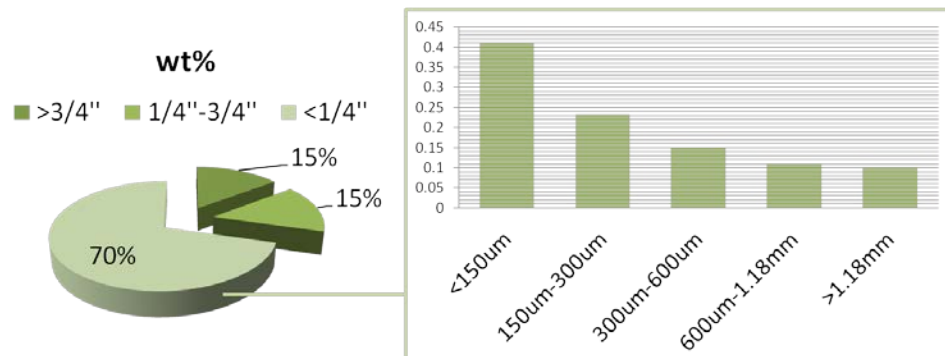


Figure 10: Size distribution of Type I dross.

And for Type II dross samples, because large pieces are too hard to break down, only the original granular portion is considered for size distribution.

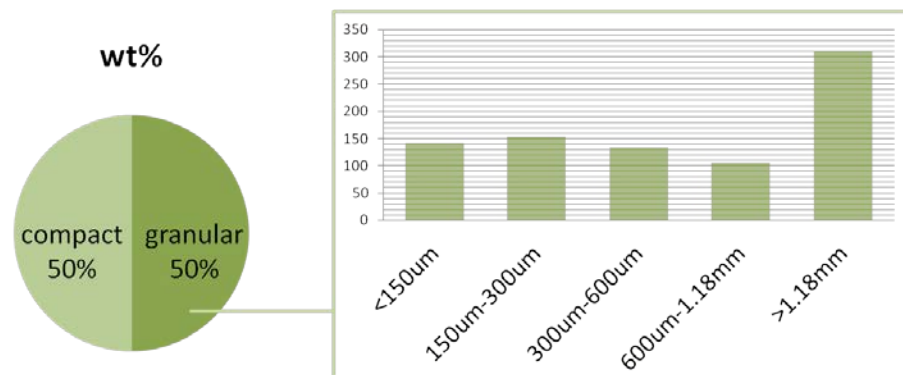


Figure 11: Size distribution of Type II Dross.

5.1.3 Density

As we can see from the table below, the compact dross has a higher density than the granular dross. Recall from the morphology part, we can find some relationship between these two different forms. With the increase of metal content, a change in the morphology takes place, and the appearance of dross is converted from granular to compact. The density increase can be explained by the agglomeration of fine portion. The liquid (melted aluminum) fills the space between particles (oxides films) and the capillary forces affect the particle coherence throughout the whole granules. Then the solid particles are coated with the liquid and form large blocks together.

Table 5: Bulk density and apparent density for both Type I and Type II samples.

Density	Granular Dross	Compact Dross
Type I	0.791-1.234 (bulk)	1.277-1.625 (apparent)
Type II	0.838-1.118 (bulk)	2.396-2.528 (apparent)

5.1.4 Leaching test

The results of leaching test characterize the behavior of the dross when coming into contact with water or moisture. The PH values are different between the two kinds of dross (Type I and Type II) and two forms (granular and compact) of dross.

Bubbles are observed coming up in each group of dross samples, which means gas releasing reactions are going on with the dross and the water. PH values of the solutions are all over 7, which means alkaline. Generally, Type II gets a higher value (10-11) than Type I (9-10). And the range of variation is different between granular form and compact form in both cases. Granular dross shows a higher salt content and more gas emission compared to compact dross.

5.1.5 Microstructure

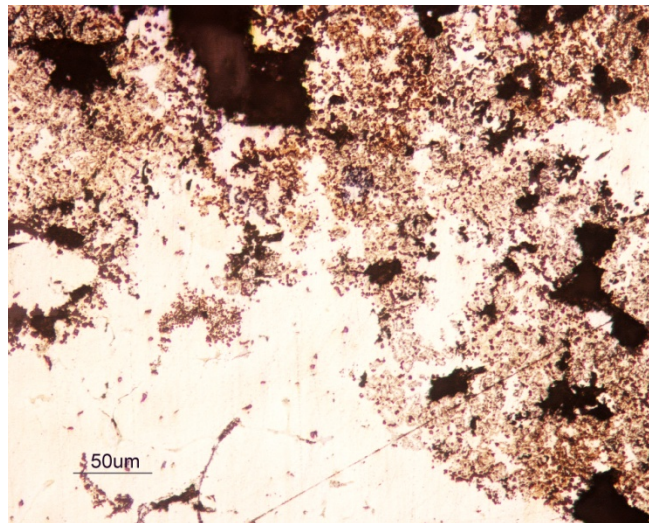


Figure 12: Optical microstructure image of Type II compact dross.

Figure 12 is a typical view of cross section of a piece of compact dross. The dark part in the picture is the mounting power, and the very bright part is the core of the compact piece. From my

point of view it is metallic aluminum, which is verified by EDS analysis later. And the regions between the above two are dendrites formed by many granular particles. What we can get from this point is that the most important reason for metal losses is not the oxidation of aluminum, but the entrapment of liquid metal and agglomeration of oxides films.

The SEM images for both Type I and Type II fine fraction are presented in 5.1.7.

5.1.6 Micro hardness

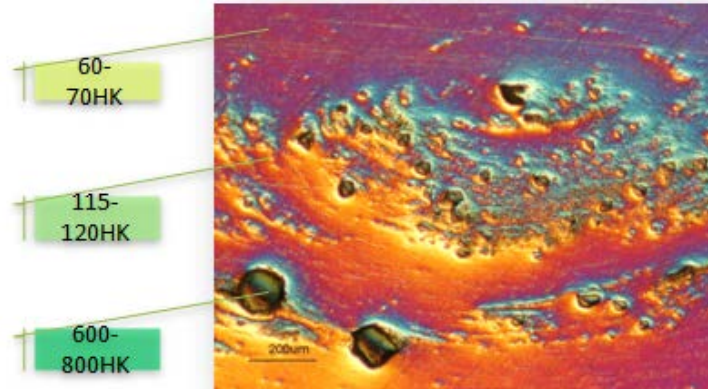


Figure 13: Microstructure and micro-hardness of samples made via FSP technique

Since the small diamond probe could punch wherever we like to test the micro-hardness, 3 kinds of places are tested. First one is an area without any dross particles; the hardness of such area is round 70HK. The area with dross particles dispersed has hardness around 120HK, which is 80% higher. Thirdly, several big particles are chosen to be tested on; the numbers are as high as 800HK, over 10 times higher than the pure alloy, which shows the potential for dross composite material to become a wear application. Similar results are gained both by Type I dross and Type II dross.

5.1.7 Chemical composition

First, SEM and EDS are introduced into the experiment for the element details. Note that in this part, only samples of granular dross are tested.

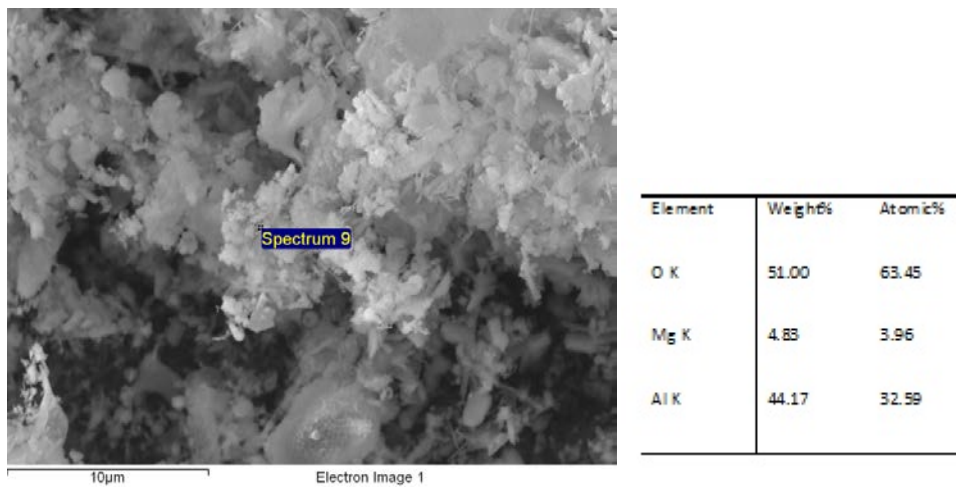


Figure 14: SEM image and EDS element analysis for Type I dross.

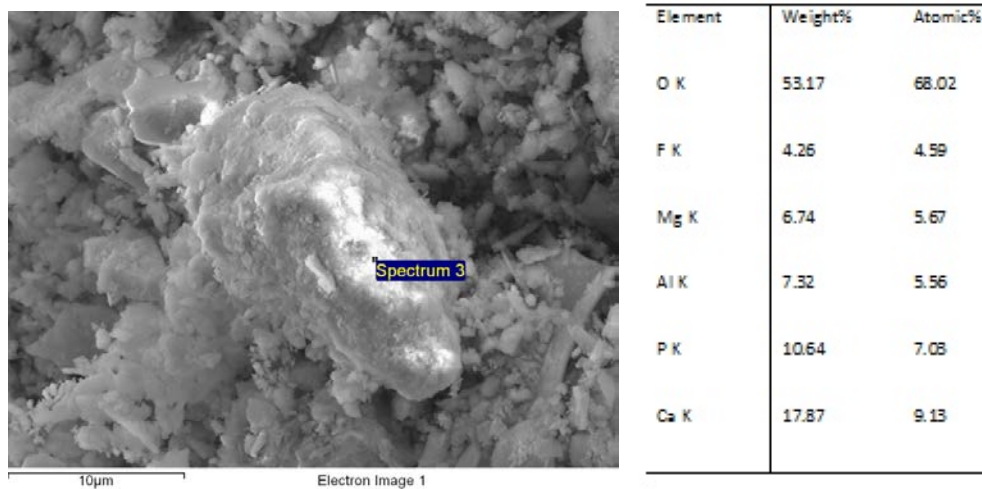


Figure 15: SEM image and EDS element analysis for Type II dross.

Clearly enough, Type II dross is a more complex mixture of all kinds of impurities. Moreover, the element constitution offers great insights for matching peaks and identifying compounds of XRD analysis.

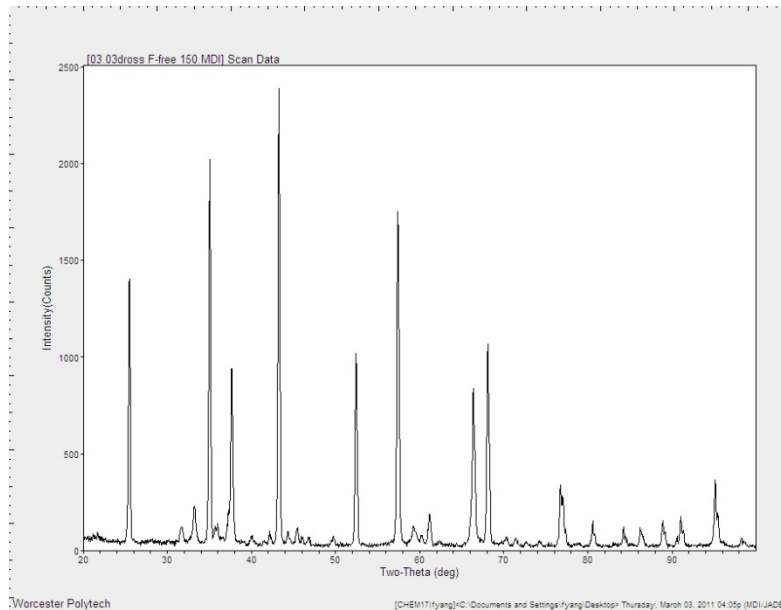


Figure 16: X-Ray Diffraction Peaks for granular dross (<150µm) of Type I.

Figure 16 is obtained from Type I dross with the particle size less than 150µm. Particles with the size of 150-300µm and 300-600µm come up with very similar figure as shown above. In the picture the major phase is certainly corundum (alumina). And as trace phase analysis proceeded, it might be AlN and the FOM (figure of merit) appears as low as 8.5. In general, a hit is very likely to be true if its FOM is less than 10.

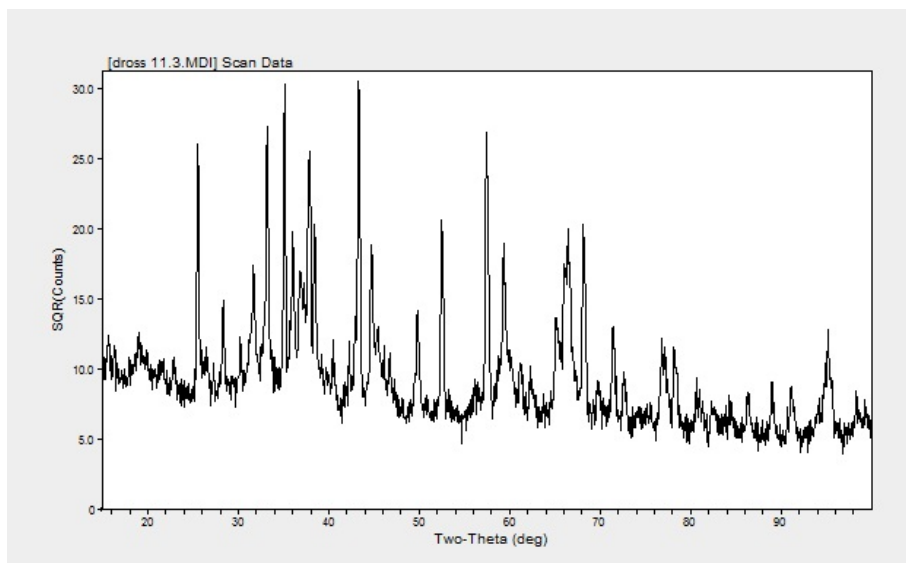


Figure 17: X-Ray Diffraction Peaks for granular dross of Type II.

Comparing Figure 16 and Figure 17, the latter has a more complex composition. Those main peaks show the existence of Al_2O_3 , AlN , MgAl_2O_4 and probably also NaCl , MgF_2 , etc.

5.2 Conditioning/Preparation

Preliminary experiment in the aspect of morphology shows that samples with large blocks tend to have more metallic metal and those with small granules usually get a higher percentage of alumina. In order to remove the salts in dross, both kinds of dross were processed with boiling water. Then XRD is used to reveal chemical compositions.

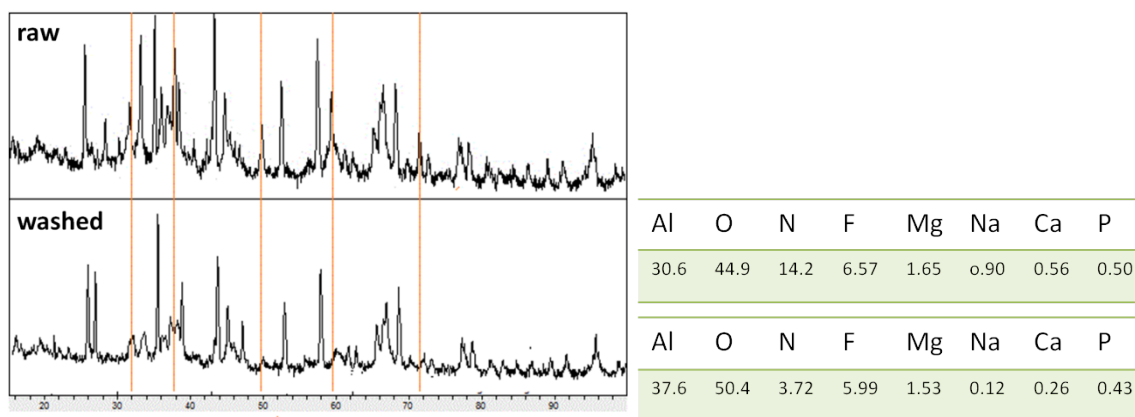


Figure 18: Comparison of the chemical composition of the raw material and washed material of Type II dross.

Figure 18 shows the XRD and EDS results of both as received case (AR) and washed case (ARW) for Type II dross. For Type I dross, there is no significant change between raw material and washed material. However, changes can be observed for Type II dross. The orange lines marked the position of aluminum nitrides. It can be observed that there is a decrease of intensity in these places after washing. As evidence, the main component of the final product is aluminum

oxide. This is because aluminum nitride, almost as important as aluminum oxide in the as-received product, has been hydrolyzed to Al_2O_3 during the heating treatment in water:



5.3 Refractory Material

5.3.1 General view

Table 6: Experiment matrix with general feasibility results.

Samples							
AR				ARW			
Type I		Type II		Type I		Type II	
<150 um	20% X	<150 um	20% X	<150 um	20% ★	<150 um	20% ★
	10% ★		10% X		10% ★		10% ☆
150-300 um	20% X	150-300 um	20% X	150-300 um	20% ★	150-300 um	20% ★
	10% ★		10% X		10% ★		10% ☆
300-600 um	20% X	300-600 um	20% X	300-600 um	20% ★	300-600 um	20% ★
	10% ★		10% X		10% ★		10% ☆

Here is a matrix (Table 6) showing all the experiments I did for concrete, including as received (AR) and washed (ARW) particles of both Type I dross and Type II dross in different adding ratios. Basically, the experiments are set to find out whether they can form a dense body. Those that expand a lot in the mold with an unacceptable up-lifting surface and a loose structure are considered to be failed case. And those marked with solid stars are the ones that have flat surfaces and dense structures. Precisely, the ingredients are not apt to segregate during blending and it causes homogenous mixture of all the components during concrete hardening. We found that all as-received Type II dross samples were out and all washed Type I dross samples produced acceptable results. The remaining experiments will focus on groups with solid stars.

5.3.2 Water-cement ratio

Water-cement ratio is the weight ratio of water and cement used in a concrete mix and has an important influence on the quality of concrete produced. Since fine dross particles have been added into the recipe as an aggregate, it is not counted into cement in calculating water-cement ratio.

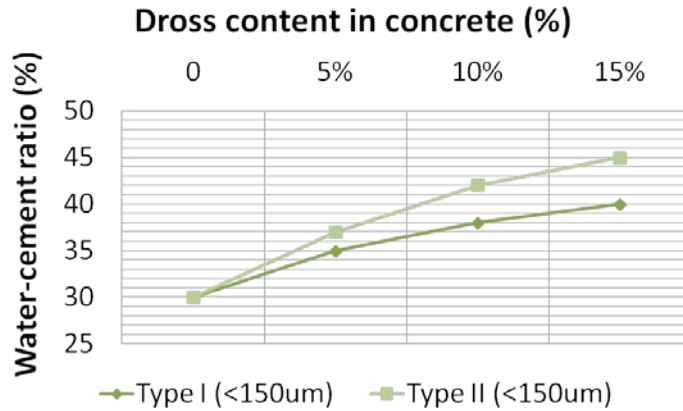


Figure 19: Different Water-Cement Ratios Between Type I Dross and Type II Dross.

As shown in the picture, there is an increase in water with the increase of the fraction of aluminum dross waste. This is because that a fraction of added water has been consumed by the reaction with AlN that forms ammonia. Note that the raised surface we mentioned before is always associated with a strong smell caused by large amount of ammonia gas. And the hydrogen reaction also has different impacts on the performance of different samples, as it can be seen that big particles, which contain more metallic aluminum usually release more gas than the smaller particles. This comparison helps understand the true mechanism and points out the necessity to sieve dross to different sizes.

5.3.3 Type I Dross vs. Type II Dross

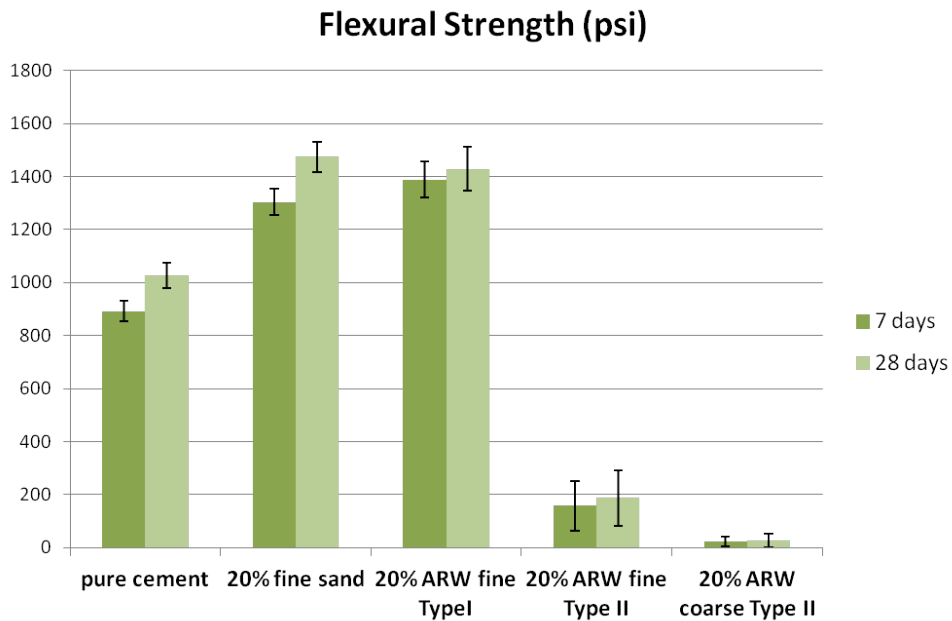


Figure 20: Flexural strength comparison of control group, Type I dross and Type II dross.

Figure 20 shows a comparison of flexural strength among concrete samples with different ingredients with the same adding ratio of 20%. Note that all values shown in the figure are mean

values of 6 tests and the error bars are set to match the standard deviation representing the viability of all the samples. The left two are control groups: one is CG_0 with no dross particle and the other is CG_i specially made for this set of groups which contains 20% fine dross powder. All samples showed an increase in 28-days testing, which is a normal phenomenon with concrete since we can expect them to reach their peak after 28 days of curing. The strength of samples in Type II group appears remarkably low, either with fine particle or coarse particle. However, Type I group stands out with higher a flexural strength than the CG_0 and its CG_i .

Although it is difficult to measure porosity precisely in our lab, differences can be seen in fracture surface and density. Huge density and volume differences can be observed in Figure 21.

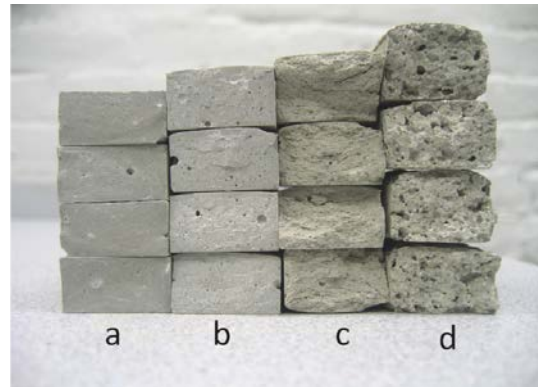


Figure 21: Fatigue surface comparison of (a) pure cement, (b) 20% ARW Type I, (c) 20% ARW fine Type II and (d) 20% ARW coarse Type II.

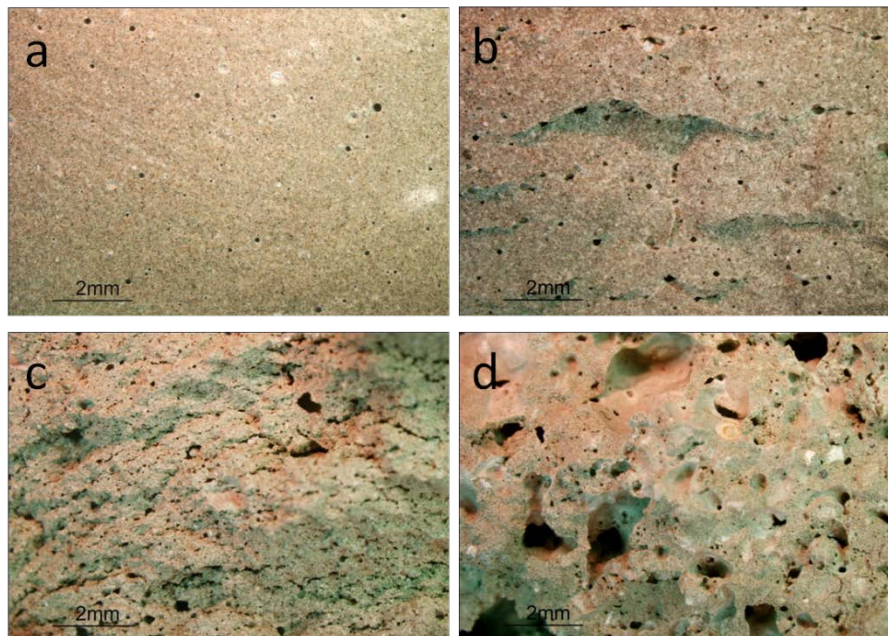


Figure 22: Microstructure and density comparison of (a) pure cement/ $\rho=2.105 \text{ g/cm}^3$, (b) 20% ARW Type I/ $\rho=2.026 \text{ g/cm}^3$, (c) 20% ARW fine Type II / $\rho=1.578 \text{ g/cm}^3$ and (d) 20% ARW coarse Type II/ $\rho=1.069 \text{ g/cm}^3$.

Comparison of microstructure can reveal more differences among these samples. Unlike the first image of pure cement, the last image shows too many pores in various sizes and shapes. No wonder its density is only half that of pure cement. On the opposite, the sample of Type I group shows a more uniform fracture surface. The slightly uneven surface revealed how the brick broke during the bending test, namely the flexural strength test, which may explain why it has a higher bending strength than the pure cement with a flat fracture surface.

5.3.4 Effect of dross fraction

Based on the previous results, it can be concluded that Type II dross has poorer performance than Type I dross; hence the following sessions will focus on Type I dross alone.

A comparison of samples has been made with different fractions of fine washed Type I dross. Figure 23 presents both compressive strength and flexural strength. Surprisingly, both properties of the 10% Type I samples are higher than that of control groups (CG₀ and CG_i). It is really encouraging, because it showed an improvement resulted from adding dross. And for the 20% sample, although there is a 12% sacrifice in compressive strength, its flexural strength is even higher.

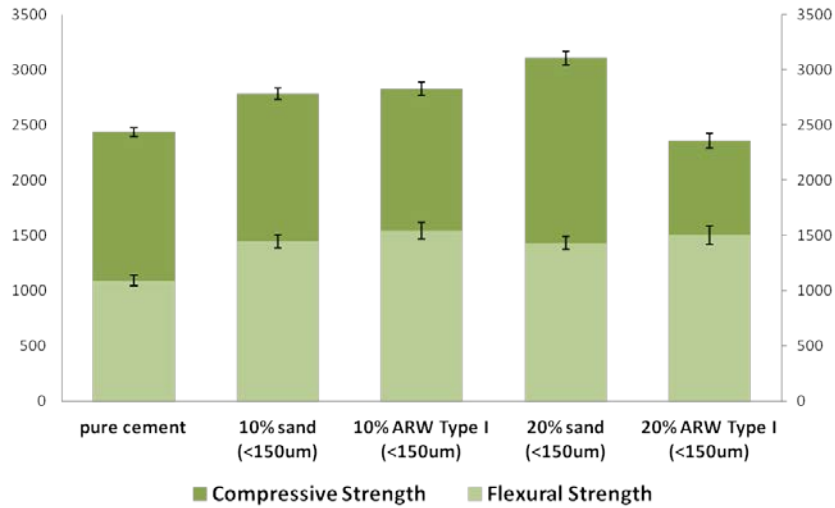


Figure 23: Compressive and flexural strength comparison (psi).

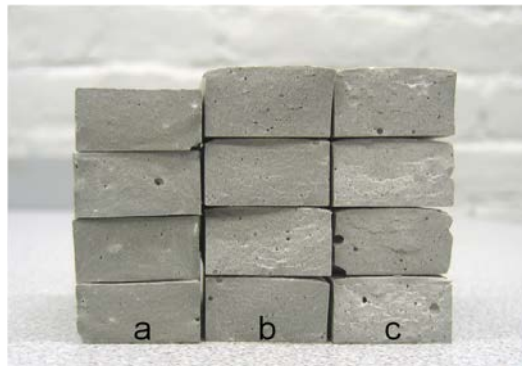


Figure 24: Fatigue surface comparison of (a) pure cement, (b) 10% ARW Type I dross and (c) 20% ARW Type II dross.



Figure 25: Comparison of microstructure and density among (a) pure cement, (b) 10% ARW Type I dross and (c) 20% ARW Type II dross.

Comparisons of microstructure (Figure 25) are also provided for these samples. It shows that the 10% fine Type I sample has a property between that of the pure cement and that of the 20% ARW sample, with more fine pores and a little fluctuation on fracture surface. In these cases, the volumes do not change much and the bulk density remains almost the same as that of pure cement.

5.3.5 Effect of dross size

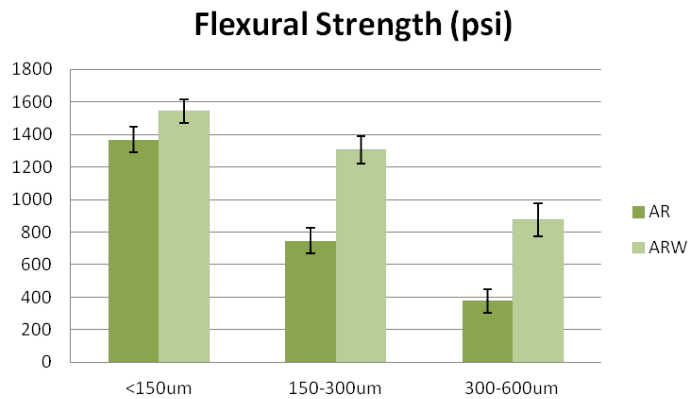


Figure 26: Flexural strength comparison of different dross sizes using AR/ARW Type I dross (10%).

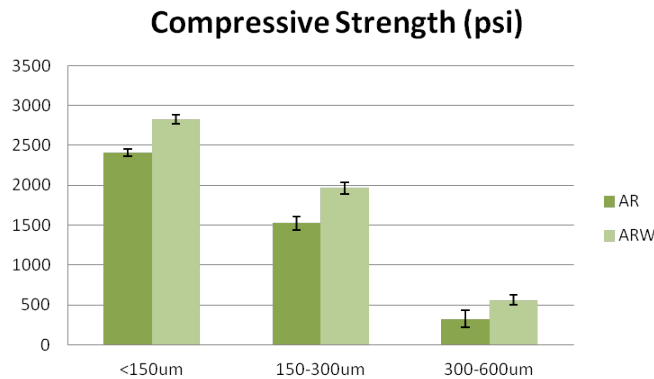
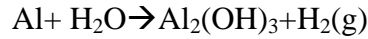


Figure 27: Compressive strength comparison of different dross size using AR/ARW Type I dross (10%).

Then comparison is made for the performance of samples using dross with different sizes. In this set of experiments, the percentage of added dross is fixed to 10% and it is still only Type I dross. The light green columns represent washed dross powder (ARW) and the dark green ones are as received powder (AR). The compressive strengths of ARW samples are always higher than those of AR samples. And both AR and ARW samples show a reduction in compressive strength with the increase of particle size. This is probably due to the hydrogen releasing reaction:



Comparing the compressive strength of medium-sized samples with that of pure cement shown in Figure 20 and Figure 28, we can see that medium-sized samples have a higher bending strength and 20% lower compressive strength, which is still acceptable.

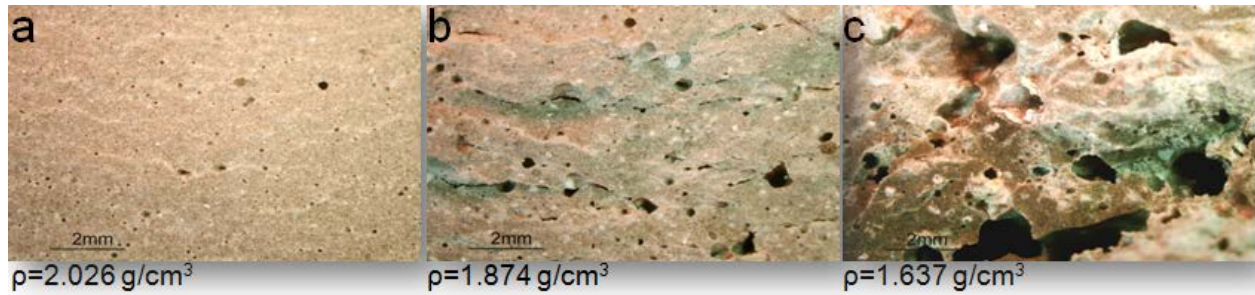


Figure 29: Microstructure comparison and density of (a) $<150\mu\text{m}$, (b) $150\text{-}300\mu\text{m}$ and (c) $300\text{-}600\mu\text{m}$ using ARW Type I dross (10%).

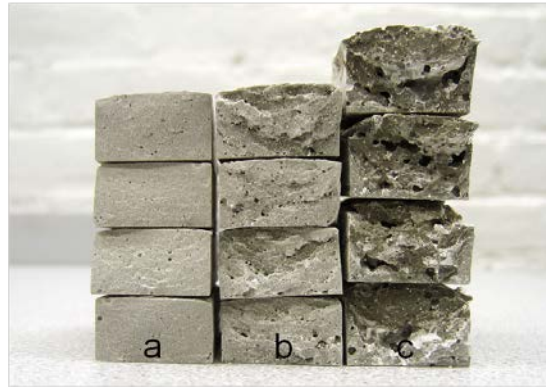


Figure 30: Fatigue surface comparison and density among (a) $<150\mu\text{m}$, (b) $150\text{-}300\mu\text{m}$ and (c) $300\text{-}600\mu\text{m}$ using ARW Type I dross (10%).

The exterior appearances of the tested samples are presented here in Fig.28 and Fig.29. The volumes of these samples have been changes, but the porosities of sample a and b are still acceptable.

5.3.6 Discussion

The results indicate that Al dross can replace fine structural components in refractory material, with some restrictions on the weight percentage of Al dross waste, particle size, and conditioning procedure. Several groups performed well in all the tests compared to other groups. Compared to the original cement samples, they either have better properties in both strengths (“ARW Type I,

<150 μ m, 10%”) or have one better property and one similar property (“ARW Type I, 150-300 μ m, 10%”, “ARW Type I, <150 μ m, 20%”, “AR Type I, <150 μ m, 10%). Samples with acceptable properties also include one from the as-received groups.

There are three possible explanations why “ARW Type I, <150 μ m, 10%” dross gets such a high performance:

1. *High stiffness of the aggregate*

High hardness of dross particles revealed in our preliminary work suggests high stiffness of this aggregate. When a cylinder sample is pressed, two things are happening behind the scene: one is the decreasing of void ratio, resulted from compression of the pores, and the other is the overlap of dross particles. Software simulations show that aggregates with higher stiffness will produce concrete with higher strength. This is because when dross particles overlap each other under the pressure, such material with higher stiffness can stand higher load before fracture.

2. *Fine uniform pores*

When gas is produced inside a material, affected by the interfacial behavior (surface tension and wetting angle), smaller pores tend to be more spherical. This is proved by our microstructure pictures as shown in Figure 22. And these spherical pores can afford greater force than pores with irregular shapes, because the dome shapes of the pores can convert vertical axial load to load of other directions, in the same way how arch bridges afford traffic and honey combs afford weight of their residents.

3. *The water-cement ratio*

Water-cement ratio has a dominant influence on the quality of concrete product. The common water-cement ratios are between 25% and 40%. Within this range, lower water-cement ratio usually causes higher strength while higher water/cement ratio provides better workability, the easiness to blend the paste to achieve homogeneous structure. In our case, we need to add enough amount of water, usually exceeding the normally maximal edge, to achieve a homogeneous structure. A tricky thing is that, fortunately, those gas releasing reactions consume parts of the water and consequently lower down the water-cement ratio within the body. Also, calcium oxide in Portland cement will react with aluminum oxide wrapped on dross particles to form $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (tricalcium aluminates). And water molecules will be absorbed by and bonded with the compound to form bond water during hydration reactions. So finally, water-cement ratio is likely to be reduced from 40% to 30%, resulting in a higher strength.

In real industrial cycle, half of the dross can be processed as Type I. After milling, 70wt% of Type I dross is less than one quarter inch. Using sieving, we can retrieve the particles less than 300 μ m, which constitutes 64wt% of it. In general, about 22.4wt% (the percentage may vary from different plants) of the total weight can be used in concrete material after simple washing procedure or even as received.

It is not easy to define the application for our dross-based concrete based on only compressive strength and flexural strength. But for concrete, other properties, such as modulus of elasticity, tensile strength, and shear strength, are usually somehow related to these two properties. Since our dross concrete has similar properties as our control group, they could also have similar applications. In our control group, we are using Type I Portland cement. It is general purpose

cement suitable for common uses where special properties of other types are not required. Its applications in concrete include pavements, floors, reinforced concrete buildings, bridges, tanks, pipes, etc. Since the dross concrete samples are better in compressive strength and flexural strength, they may have a better performance than control groups.

5.4 Aluminum Composite

Although the current discontinuously reinforced metal-matrix composites (DRMMCs) have a number of attributes that make them attractive to the automotive engineer, they are still too expensive to be used in mass production, especially for the class of advanced structural materials. A costly reinforcement of a metallic matrix by ceramic particles usually leads to a less profitable improvement of overall material properties.

Since dross is an industrial waste that is cheap to obtain, it would be nice if using it in aluminum composites can provide higher strength, thus creating DRMMCs as structural materials with competitive quality-cost ratio.

For composite material, strength improvement depends on the ability of transferring ring stress from the matrix to a stronger reinforcing phase. One of the effects is the change of microscopic properties, including well-dispersed phase in microstructure and high value of micro-hardness. These changes are presented below for both FSP experiment and casting experiment.

5.4.1 Friction stir processing

Friction stir processing is applied to dross particles using A206 as the matrix. Figure 16 is the view through optical microscope; it can be seen that particles dispersed along the stirring direction. The results of micro-hardness can also be found in section 5.1.6.

Also, the samples are tested by scanning electron microscope (shown in Figure 30). Sizes of most particles are about 2 microns. Note that the milling processing has been done by hand using a hammer. If a milling machine is used to crush the dross, the particle sizes will be more uniform and more controllable.

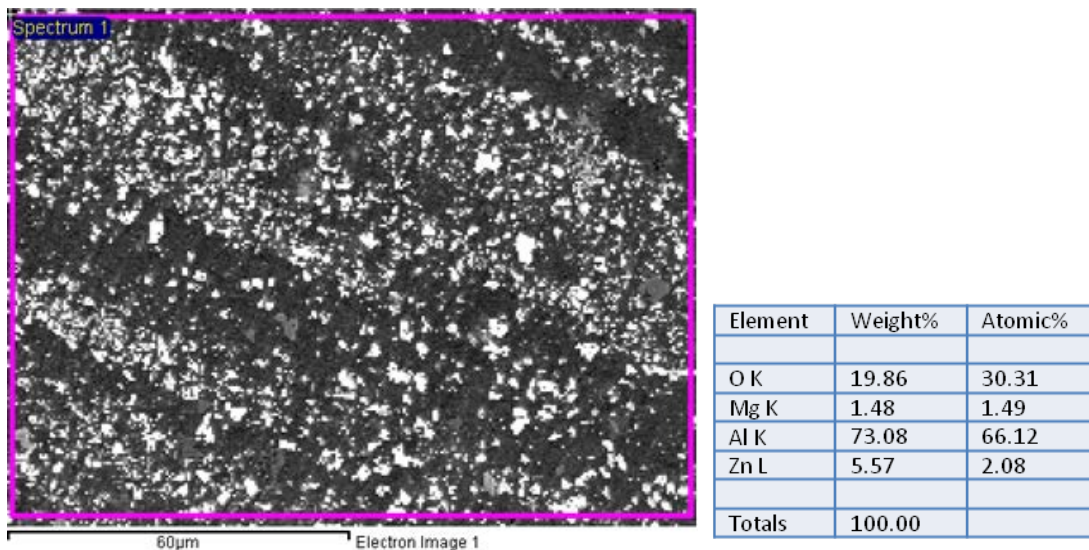


Figure 31: Microstructure and element composition obtained by SEM and EDS.

In another measurement, EDS analysis was applied to show element constitution. If we select area like Spectrum1 in Figure 30, as the composition include elements of oxygen, magnesium, aluminum and zinc. Compared to the matrix composition (94.43%Al, 4.60%Cu, 0.25%Mg, 0.35%Mn, 0.05%Si, 0.22%Ti, and 0.10%Fe), dross may contain all these four elements. If we do the composition test right on one of the dross particles in this picture, it seemed to be purely oxygen and aluminum. As I did never wash the dross samples or perform any other conditioning process, the only explanation is that the contents of other elements are lower than the minimum percentage that EDS can detect. The compositions in different area throughout the whole sample are almost the same with only small variation. This means that the dross particles are well dispersed in these regions, which is a good sign for composite material.

5.4.2 Casting

In the casting experiments, most of the samples end up with too many pores and cracks. Only one sample showed something interesting: Sample E reveals a new possible existing form of dross, which is different from what phase diagram tells us. In the optical microscope picture (Figure 31), there are always a bunch of black dots on the second phase (rich in silicon), which is quite different from the texture of pure A356 shown in the literature.

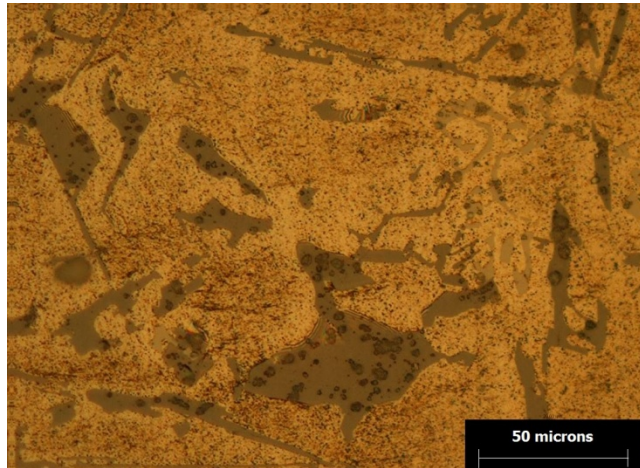


Figure 32: Microstructure of Sample E (alternative layers).

In a zoomed-in view under the SEM (Figure 32), the results obtained by EDS shows that the main component of these particles is alumina (Spectrum 3), and fluoride from dross tends to appear with precipitates rich in silicon (Spectrum 2).

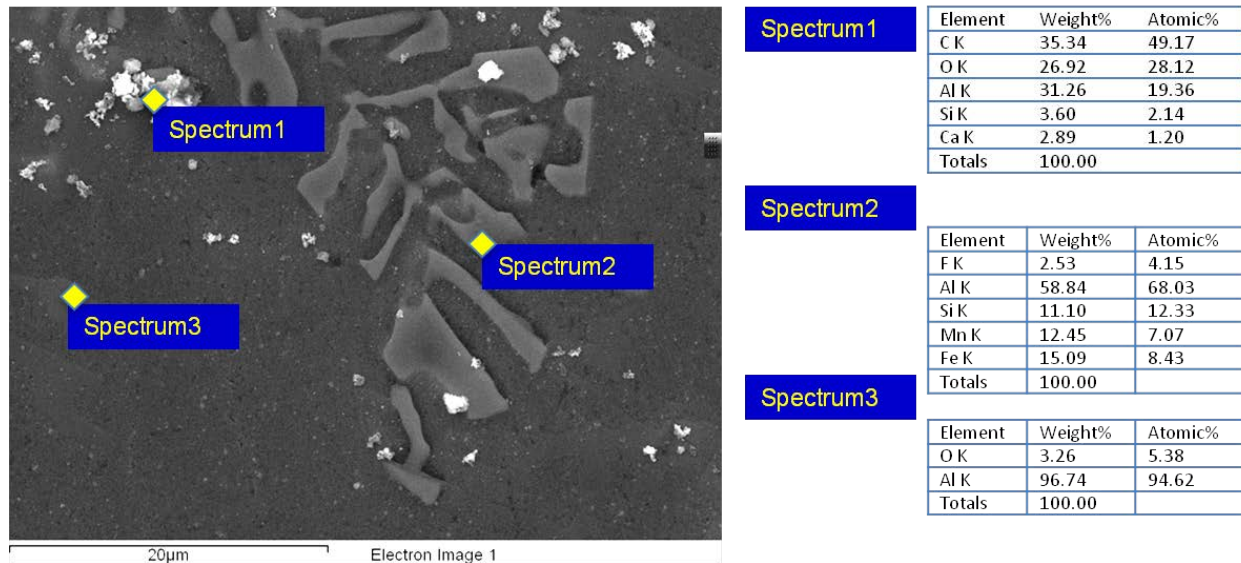


Figure 33: SEM image of Sample E along with element composition on the right.

The Particle size and the segregation (on the second phase) prove that these particles are not polishing powder, which means these particles must be dross powder. This tells us that either dross can benefit the nucleation of second phase particles or dross tends to attach on second phase particles. In either case, the observation that dross particles usually appear together with second phase particles indicates that dross particles are well dispersed in the whole matrix, since second particles are well dispersed in the matrix. However, this hypothesis needs more well designed systematic experiments to justify.

5.4.3 Discussion

The results above indicate that aluminum dross has a potential to be a cost-efficient reinforcement for structural aluminum-based composites. Two key properties to determine the feasibility of this approach are tensile strength and wear resistance.

The tensile strength of metal matrix composites will be influenced by two independent mechanisms. One is the load transfer from the soft matrix to the rigid reinforcement [29, 30]. The other the increase of dislocation density caused by the mismatch between matrix and reinforcement particles. Generally, we can predict that the increase in strength is affected by the volume fraction, dispersion degree and size of dross particle. To be more precise, larger fraction, higher dispersion degree and smaller size will provide a better strength.

On the other hand, composites with coarse dross particle are also competitive for wear applications in some less critical engineering components. The high hardness of dross particle will lead to a superior wear resistance, indicating, from a technical point of view, that these composites may be considered as replacements of cast iron in large production of brake rotors and brake pads.

5.5 Comparison between Concrete material and Al Composite

So far, we have looked at results from the concrete experiment and the aluminum composite experiments. And it is time to reflect on why dross powder has such a poor performance in metal compared to the performance in concrete.

First, when nonmetallic particles, such as dross particles, are added to fully molten metal, many of them are rejected and cast out onto surface of the melt because they cannot be wetted by the metal. However, in concrete paste, dross powder will go through a series of hydration reaction to form the homogenous structure.

Second, sharp edges of dross particle or pores generated by dross can easily cause stress concentration in metal matrix, and crack will begin to propagate as a result. Although adding dross particle into metal matrix can provide a 30% increase in abrasive resistance, complex processes will be needed to achieve the required uniform shapes and composition; these processes are too expensive compared to the possible benefits. On the other hand, concrete appeared to be more tolerant. Macro pores are acceptable in the matrix and they can sometimes increase the thermal insulation and density without causing strength degradation.

Also, as we can see in the experiments, it is difficult to stir dross powder into metal effectively in large scale. Well-dispersed structure requires heavy work of machining or stirring in a high temperature, which means huge consumption of extra energy. On the other hand, homogenous concrete paste is easy to achieve with a simple blender.

Last but not the least, metals and alloys are more precious than pure metal and they are often designed for higher requirements. It is reasonable to add pure and well manufactured alumina powder or silicon carbide powder to it to enhance their properties in order to guarantee their special applications. On the contrary, a large number of basic applications of concrete can be found without high requirements.

6. CONCLUSIONS

Dross is produced in a significant volume each year, and with the increased manufacturing, the volume will only increase with time. Instead of recovering the metallic aluminum from the dross, using the dross as an engineered product will be a better way of up-cycling.

In this thesis, two domains were investigated for the sake of channeling aluminum dross material towards certain applications. One was concrete material in refractories and the other was aluminum composites. Both of them were on the results of high alumina content of dross. After examining the basic physical and chemical properties, we developed a simple conditioning method involving washing with boiled water.

Two kinds of aluminum dross were tested as a replacement raw material in refractories. The results of this part indicated that dross can be applied either through a simple purification process or directly as a substitute for fine structural components in refractories. A series of experiments were carried out in order to investigate the properties of dross with different types, fractions, and sizes. Although pores and defects could be generated from gas releasing reactions, the properties are still acceptable. Mechanical property evaluations revealed the possibility for dross waste to be utilized as filler in concrete, resulting in a 25% higher flexural strength and a 5% higher compressive strength compared to pure cement. Even though the fraction of Al dross waste that can be added to refractories is small, both the waste body and the potential market for reusing Al dross are huge.

Moreover, the results achieved from forming aluminum composite were also encouraging. Adding dross to metal matrix composite material was achieved via two different approaches. One was friction stir processing and the other is casting. Well dispersed dross particles were observed in the microstructure pictures, which verified the feasibility of using dross particles for strengthening. Thus, it confirmed the potential for finely powdered dross to be used as a cost-efficient reinforcement in discontinuously reinforced aluminum-matrix composites.

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