FEASIBILITY OF UTILIZING IGCC BYPRODUCTS FOR NOVEL MATERIALS DEVELOPMENT

COSMOS TECHNOLOGIES, INC.

Project Team

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  - Frederick Douglas
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Technical Assistance Provided By:

- Dr. Paul Chugh- University of Southern Illinois
- Dr. Carlo Pantano- Penn State University
- Rob Schaut- Graduate Student, Penn State University

Acknowledgements

- **William Aljoe**: Technical Support & Constructive Input
- **Tampa Electric**: Provide IGCC Byproducts Samples
- **Mr. Phil Amick** of Conoco Phillips: Tech. Discussions
- **Corning**: Tech. Discussions with Glass Experts
- **Ferro Corp**: Evaluation of the Inorganic Pigment Frit Potential
- **Dr. Paul Chugh:** Technical Guidance & R&D Assistance
- **Dr. Carlo Pantano:** Technical Guidance & R&D Assistance

Study Objectives

The overall goal of this project was to perform an exploratory study for utilizing IGCC solid by products to develop value- added novel materials beyond already explored cement- concrete applications

Specific Objectives

1.0 Characterize the Frit and Carbon- rich Fraction from a materials development point of view. This study will include thermal, physical and chemical analyses.

2.0 Based on the data from (1) above, identify at least two (2) novel applications for “medium-volume-utilization” of one or more fractions of the gasification byproducts.

3.0 Perform laboratory studies on a limited scale to develop and characterize novel materials for applications identified above.

Literature Review- Innovative Products From IGCC Byproducts

- Most of the work in this field focus on the use of IGCC Byproducts in cement, or filler in road bed construction.
- PRAXIS performed studies to develop LWA and ULWA for use in cement-aggregate applications.
- Wabash River IGCC demonstration plant, reported that the carbon vitreous slag may be used as aggregate in construction or as grit for abrasives and roofing material.

Literature Review Contd.

- Charah Environmental/ University of Kentucky demonstrated that the IGCC byproducts from TECO Energy demonstration plant can be separated into three fractions: vitreous material or frit, carbon- rich char and fines.

- Chugh and Patwardhan (2002) demonstrated a physical separation technique to separate slag from char based on size separation and flotation techniques. Studies performed for TECO IGCC byproducts.

- Norton (2004) of the University of Mississippi studied the incorporation of gasifier slag for the enhancement of structural foam glass materials.

Literature Review Contd.

- The Norton study concluded that the addition of small amounts of slag significantly increases the compressive strength of the foamed glass. The foamed nature of the frit can provide an energy absorbing barrier for impacting weapons.

- The University of Kentucky is currently performing pilot studies to separate the three major fractions of the IGCC slag. The pilot study is utilizing 100 tons of slag for this study.

Detailed Elements of Study

- Byproduct characterization studies.
- Review of pertinent literature
- Physical characterization studies- particle size distribution
- Chemical characterization- Oxides composition, limited elemental analysis
- Environmental analysis- ASTM and TCLP shake tests
- Material characterization- SEM, TGA, DSC

Detailed Elements of Study Contd.

Cosmos Technologies/ Paul Chugh- University of Southern Illinois/ Carlo Pantano- Penn State University made the preliminary determination that the following novel product or applications shows significant potential:

- Rockwool and spray insulation material for the building industry
- Fireproof glazing materials for steel structures
- Obscurance materials for defense applications

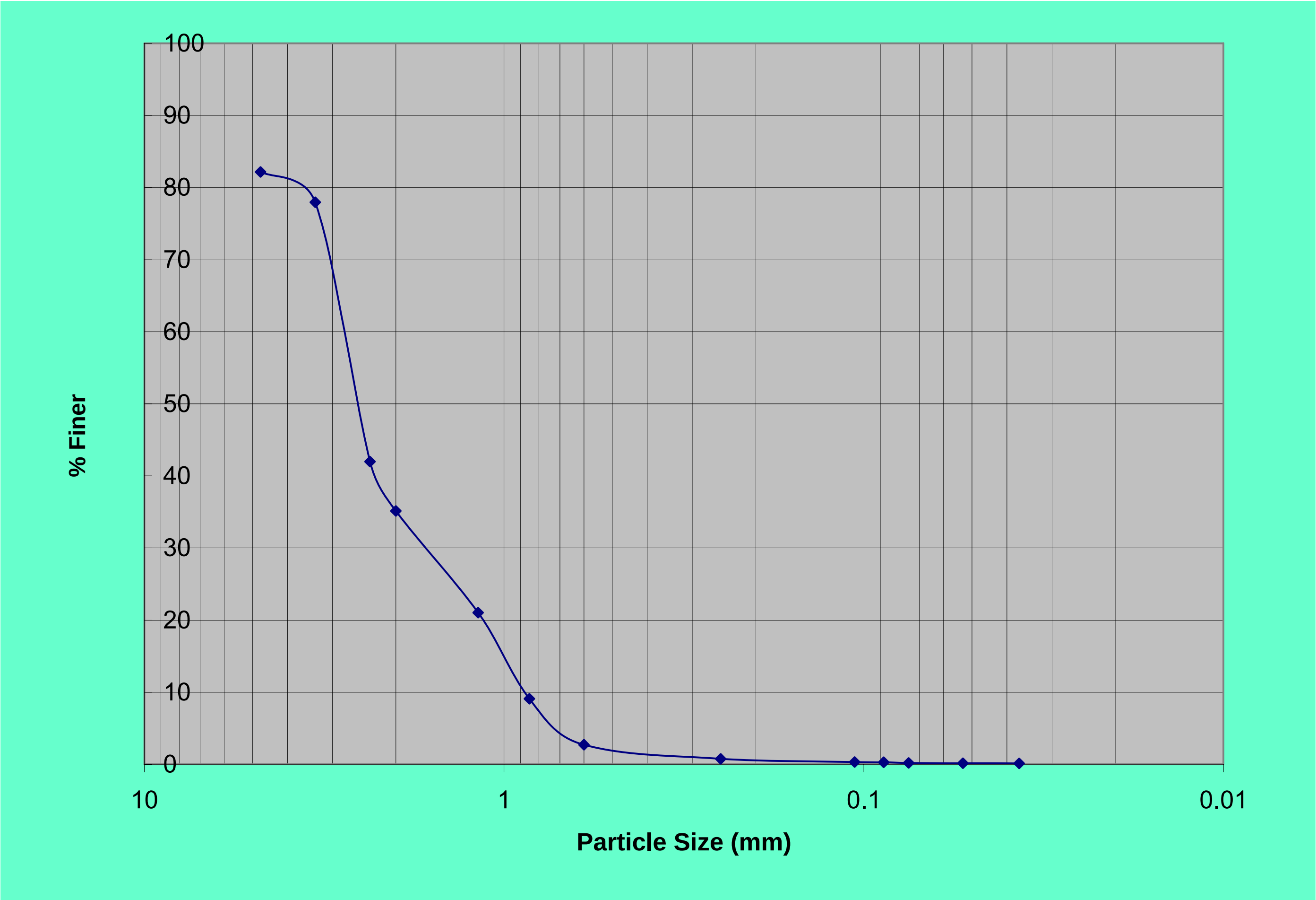
Detailed Elements of Study

- Heat sink substrate for solar or other heat collection systems
- Low weight filler
- Fluidized bed media to replace currently used synthetic ceramics which are more costly

Silica-rich (Frit) Sample

- Mean particle size for frit is 2.3mm
- Uniformity coefficient and the coefficient of gradation- 3.1 and 1.1.
- This implies that most of the particles are of uniform size.
- XRD shows the sample to be amorphous.

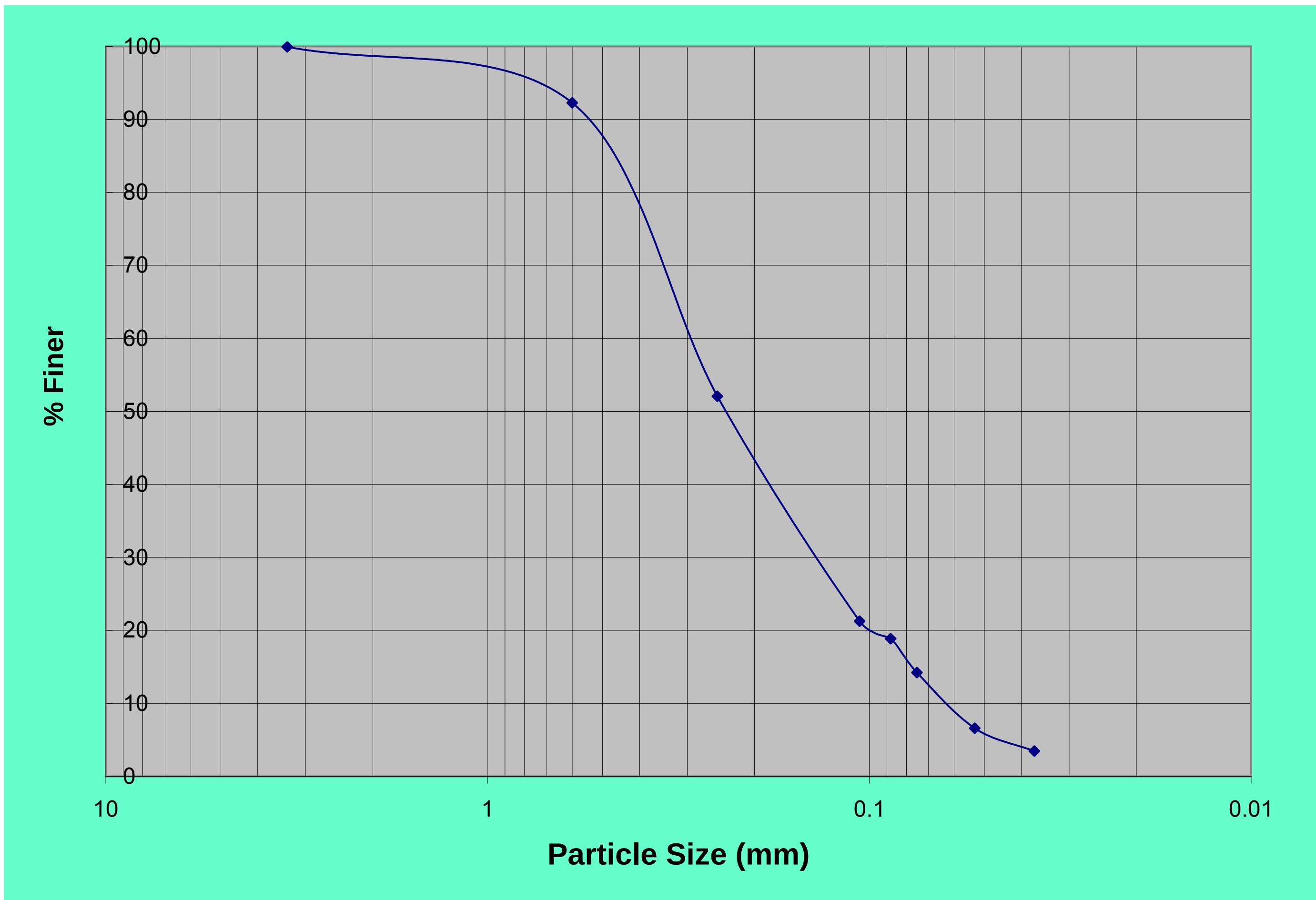
Silica Rich (Frit) Sample



Silica Poor (Carbon Rich) Sample

- Mean particle size of the carbonaceous fraction is 0.23mm.
- The uniformity coefficient and coefficient of gradation- 4.8 and 1.04.
- Most of the carbonaceous fraction particles have a wider range of particle sizes than the frit fraction.
- XRD shows the sample to be amorphous

Silica Poor (Carbon Rich) Sample



Oxides Composition

- The silica- rich sample has an average of 54.4% silicon oxide
- The silica- poor sample has an average of 26.6% silicon oxide
- The silica- poor sample has an average of 24.18% sulphur

Table 3: Oxides composition analyses

Carbonaceous Fraction			Frit	
Oxides	**Weight %**	**Std Error**	**Weight %**	**Std Error**
Na2O	1.45	0.06	3.06	0.09
MgO	0.43	0.021	0.989	0.049
Al2O3	11.27	0.16	19.87	0.2
SiO2	26.6	0.22	54.4	0.25
P2O5	0.676	0.034	0.406	0.02
Sulphur	24.18	0.21		
Cl	1.45	0.06		
K2O	2.69	0.08	2.31	0.08
CaO	2.61	0.08	3.79	0.1
TiO2	1.15	0.05	0.962	0.048
V2O5	6.84	0.13	2.56	0.08
Cr2O3	< 2*(std error)	0.033	0.095	0.012

MnO	0.0519	0.0046	0.0523	0.0026
Fe2O3	16.22	0.18	10.83	0.16
Co3O4	0.0149	0.0044	0.0135	0.0014
NiO	2.69	0.08	0.415	0.021
CuO	0.233	0.012	0.0127	0.0011
ZnO	0.577	0.029	0.0041	0.0009
Ga2O3	0.121	0.006	0.0041	0.0008
GeO2	0.0823	0.0041		
As2O3	< 2*(std error)	0.02	< 2*(std error)	0.003
SeO2	0.0527	0.0041		
Rb2O	0.0244	0.003	0.0113	0.0007
SrO	0.101	0.005	0.0551	0.0028
ZrO2	0.0621	0.0051	0.0366	0.0018
MoO3	0.181	0.009	0.0235	0.0017
PbO	0.255	0.013		

ENVIRONMENTAL PROPERTIES

Table 1: Shake test results

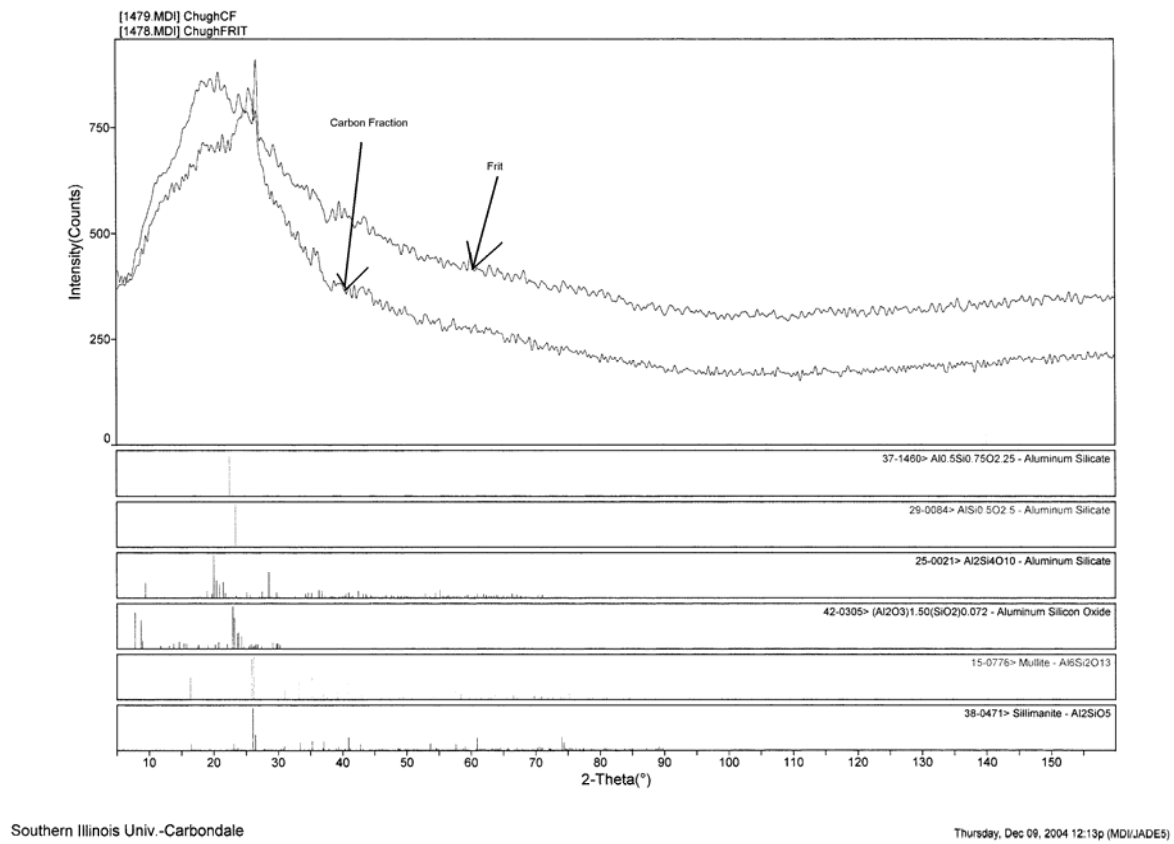
FRIT					Water Quality Standards	
Samples	**3hr**	**6hr**	**9hr**	**Standard Shake 18hour**	**Class I**	**Class II**
pH	4.19	4.45	4.37	4.37	6.5 - 8	6.5 - 8
Elements (in ppm)						
Arsenic	0.02	0.02	0.04	0.02	0.05	0.2
Boron	2.45	2.7	2.77	2.96	2	2
Barium	0.17	0.17	0.15	0.16	2	2
Cadmium	0.22	0.23	0.25	0.24	0.005	0.05
Cobalt	0.33	0.35	0.37	0.39	1	1
Chromium	0.01	0.001	0.002	0.002	0.1	1
Copper	0.48	0.34	0.38	0.32	0.65	0.65
Iron	0.74	0	0.01	0	5	5
Lead	0.34	0.01	0.12	0	0.0075	0.1
Manganese	0	0.02	0.05	0.08	0.15	10
Nickel	34.18	36.29	37.92	37.41	0.1	2
Silver	0	0	0	0	0.0075	0.1
Selenium	0.15	0.12	0.13	0.2	0.05	0.05
Zinc	14.41	14.4	14.4	14.4	5	10

Carbonaceous Fraction					**Water Quality Standards**	
Samples	**3hr**	**6hr**	**9hr**	**Standard Shake 18hour**	**Class I**	**Class II**
pH	7.5	7.28	7.28	7.04	6.5 - 8	6.5 - 8
Elements (in ppm)						
Arsenic	0.01	0.02	0.07	0.08	0.05	0.2
Boron	0	0.05	0.08	0.11	2	2
Barium	0.15	0.14	0.08	0.16	2	2
Cadmium	0	0	0	0	0.005	0.05
Cobalt	0	0	0	0	1	1
Chromium	0	0	0	0	0.1	1
Copper	0	0	0	0	0.65	0.65
Iron	0	0	0	0.01	5	5
Lead	0	0	0	0	0.0075	0.1
Manganese	0	0	0	0	0.15	10
Nickel	0.61	1.44	2.31	1.68	0.1	2
Silver	0	0	0	0	0.05	0.05
Selenium	0	0	0	0	0.05	0.05
Zinc	0	0	0	0.01	5	10

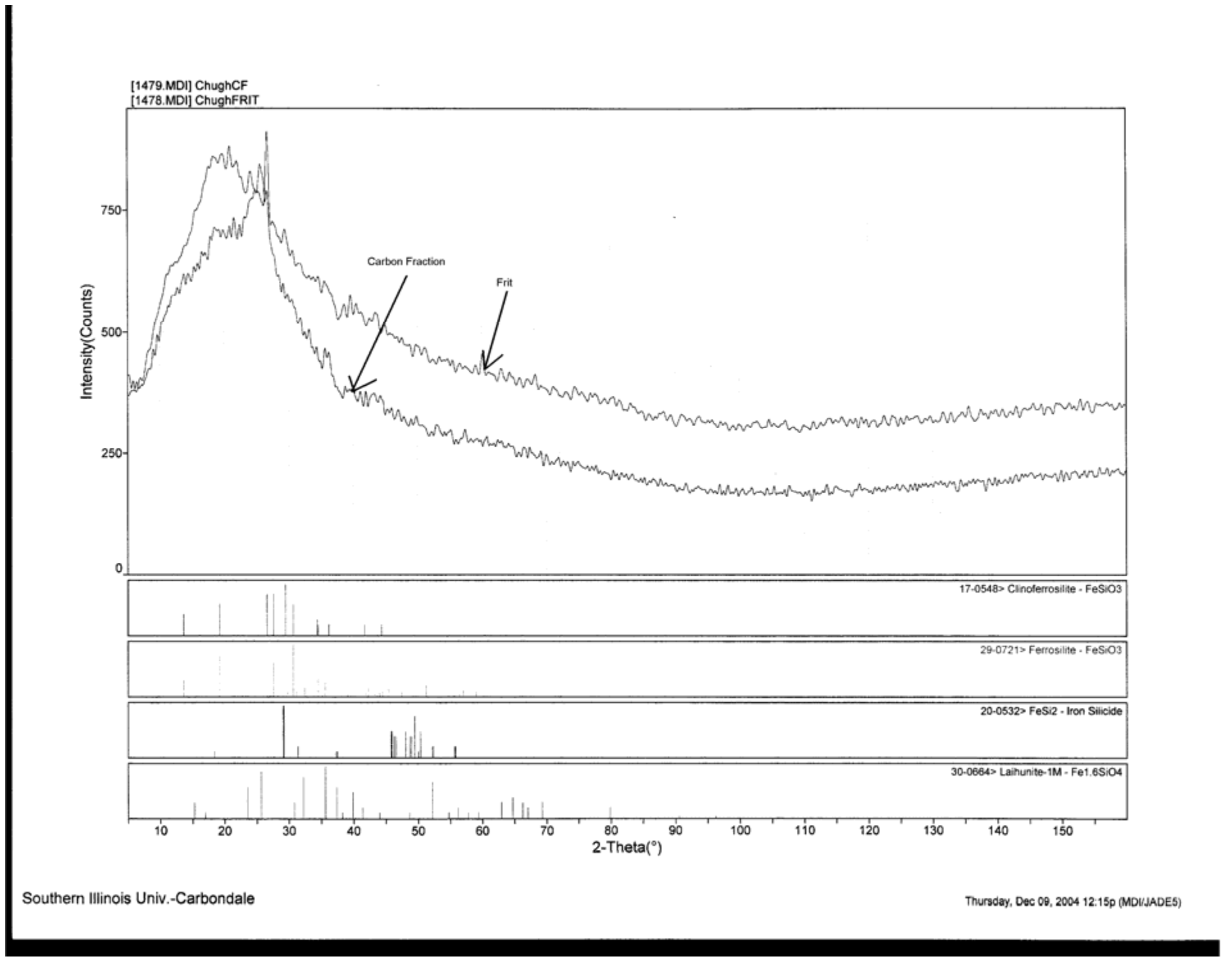
Table 2: TCLP test results

Samples	Frit	Carbon Fraction	Class I (Water quality std)	Class II (Water quality std.)
pH	4.84	4.87	6.5 - 8	6.5 - 8
Elements (in ppm)				
Arsenic	0.07	0.08	0.05	0.2
Boron	0.14	3.38	2	2
Barium	0.63	0.25	2	2
Cadmium	0	0.21	0.005	0.05
Cobalt	0.11	0.34	1	1
Chromium	0	0.02	0.1	1
Copper	0.25	0.28	0.65	0.65
Iron	10.03	0.2	5	5
Lead	0.07	0.2	0.0075	0.1
Manganese	0	0.11	0.15	10
Nickel	13.04	35.06	0.1	2
Silver	0	0	0.05	0.05
Selenium	0	0.35	0.05	0.05
Zinc	0.39	14.25	5	10

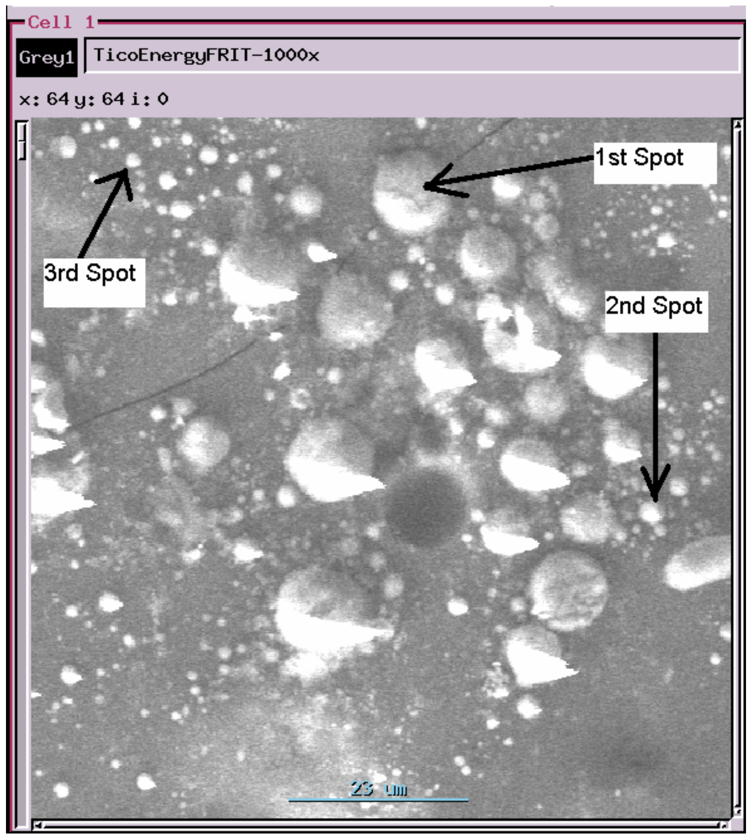
XRD Analysis of Frit Fraction



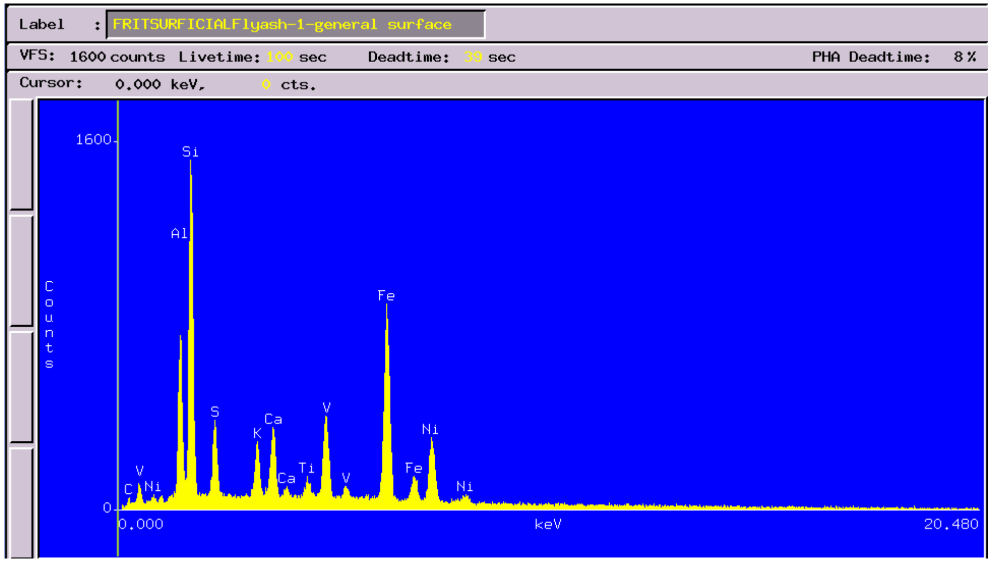
XRD Silica Poor Fraction



SEM image of Frit particle surface (1000x magnification)



EDX General Area of Frit Particle



EDX- Spot 1(Frit Fraction)

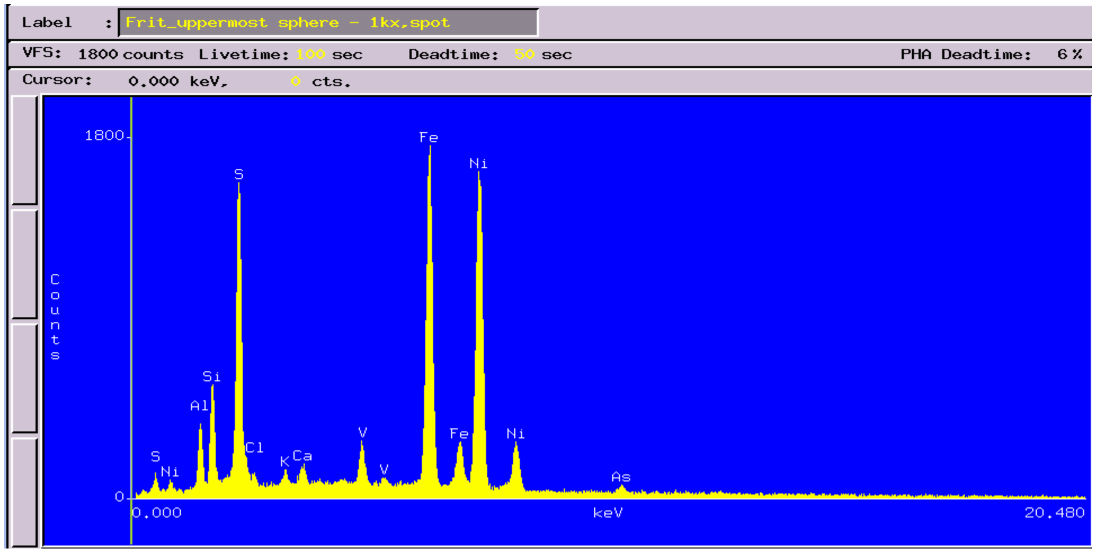
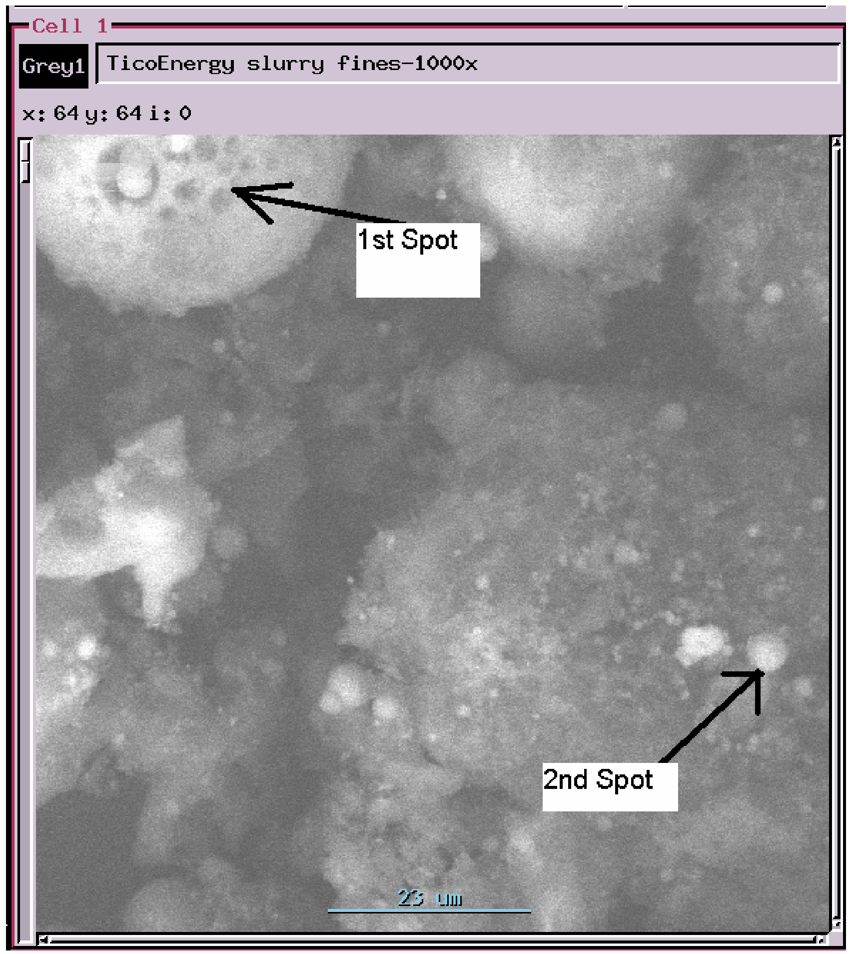
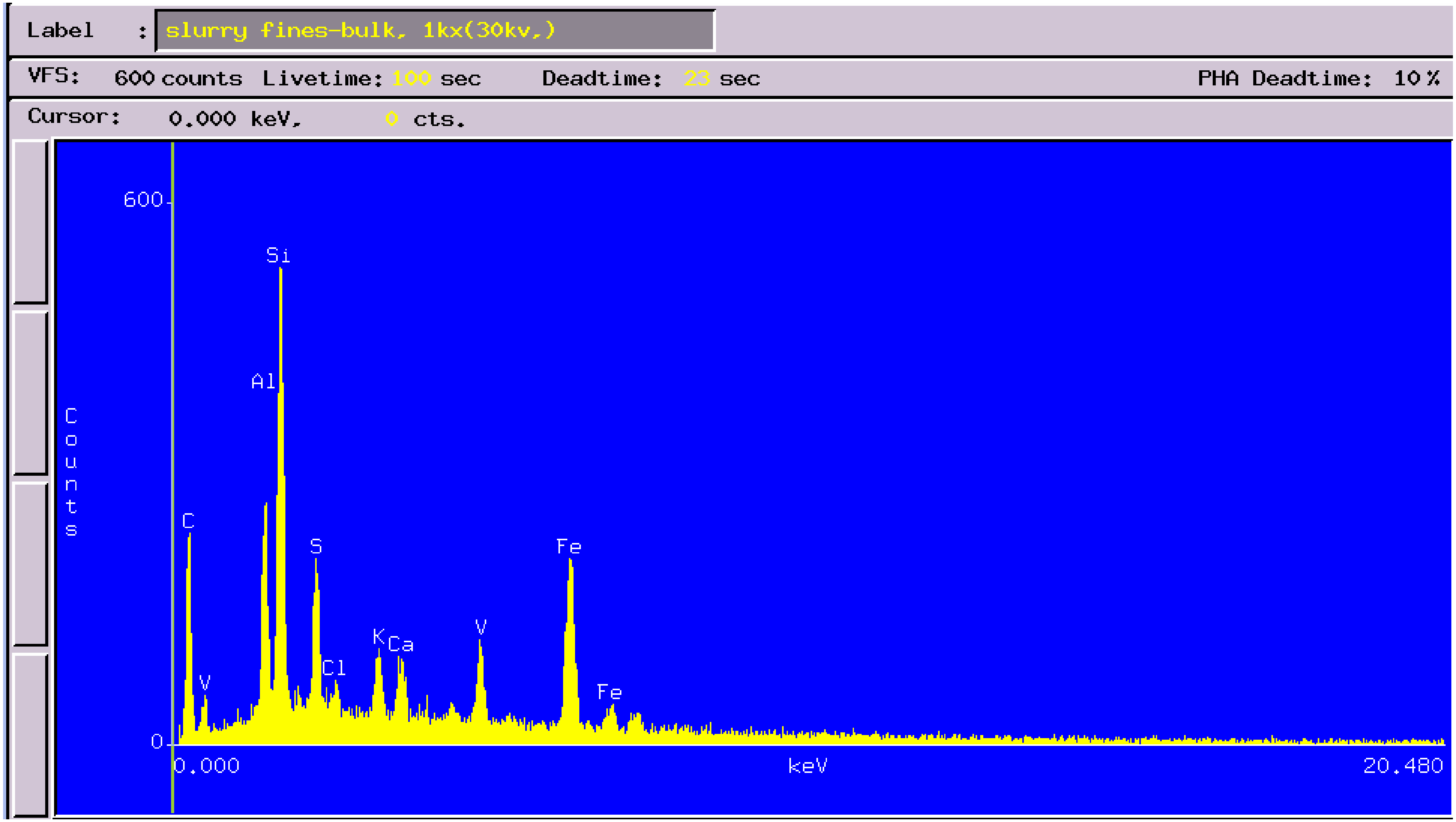


Image of carbonaceous fraction matrix (1000x magnification)

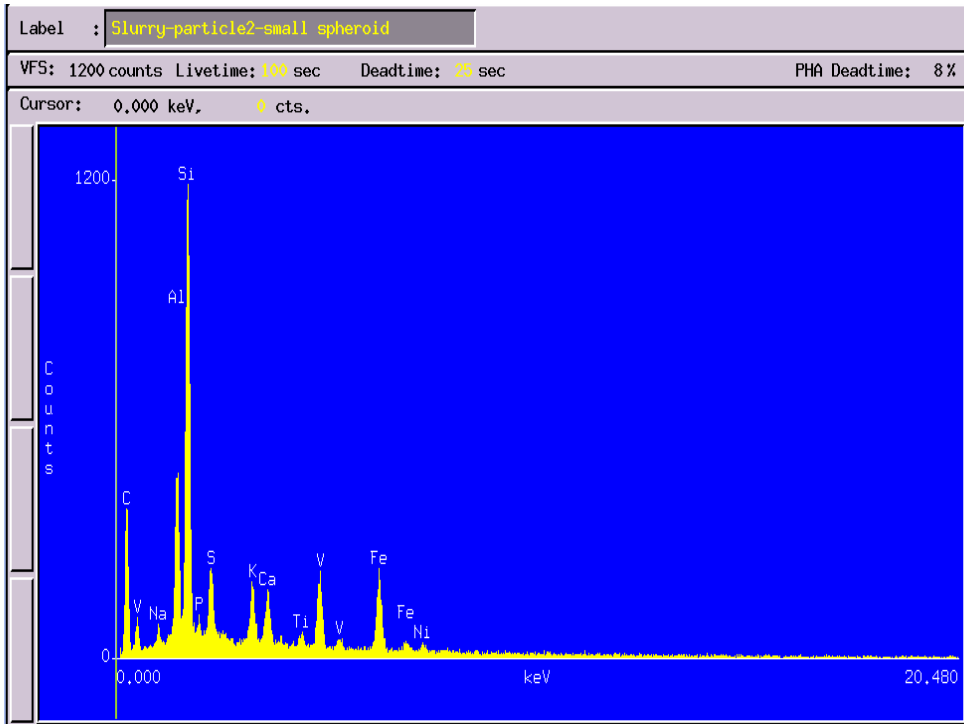


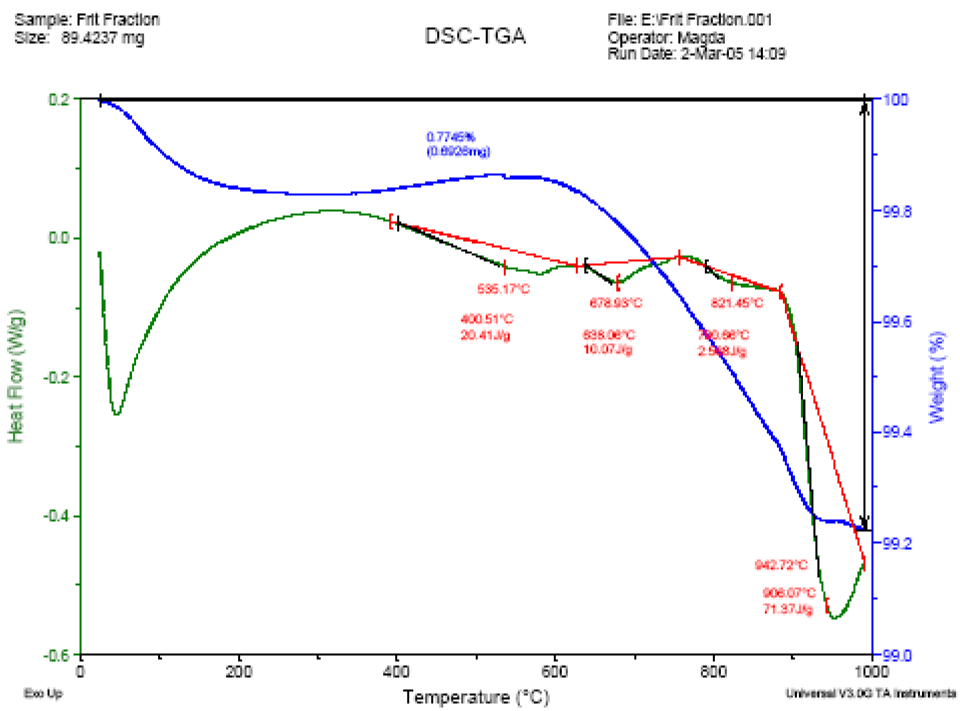
EDX General Area (Carbonaceous Fraction)



EDX of Spot 2 (Carbonaceous Fraction)

Similar to frit fraction

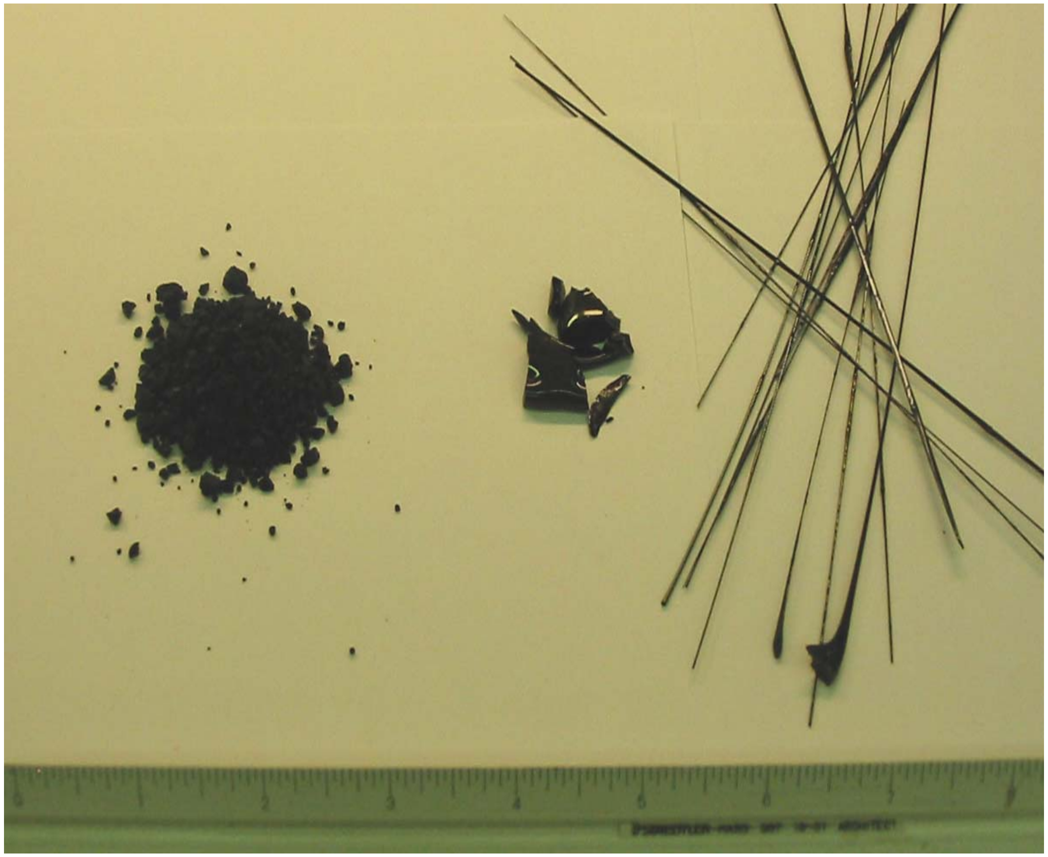



Sample: Frit Fraction
Size: 89.4237 mg
DSC-TGA
File: E:\Frit Fraction.001
Operator: Magda
Run Date: 2-Mar-05 14:09
0.7746%
(0.6926mg)
400.51°C
20.41J/g
678.93°C
10.07J/g
821.45°C
942.72°C
906.07°C
71.37J/g
Heat Flow (W/g)
Weight (%)
Temperature (°C)
Exo Up
Universal V3.0G TA Instruments

Frit for Inorganic Pigment Applications

- Evaluated vitrified fraction use as a frit (work done at Ferro Corporation)
- Vitrified material sample was grounded and then screen printed. The vitrified material did not adhere to the surface during screen printing.
- This could be due to the crystalline nature of this glass

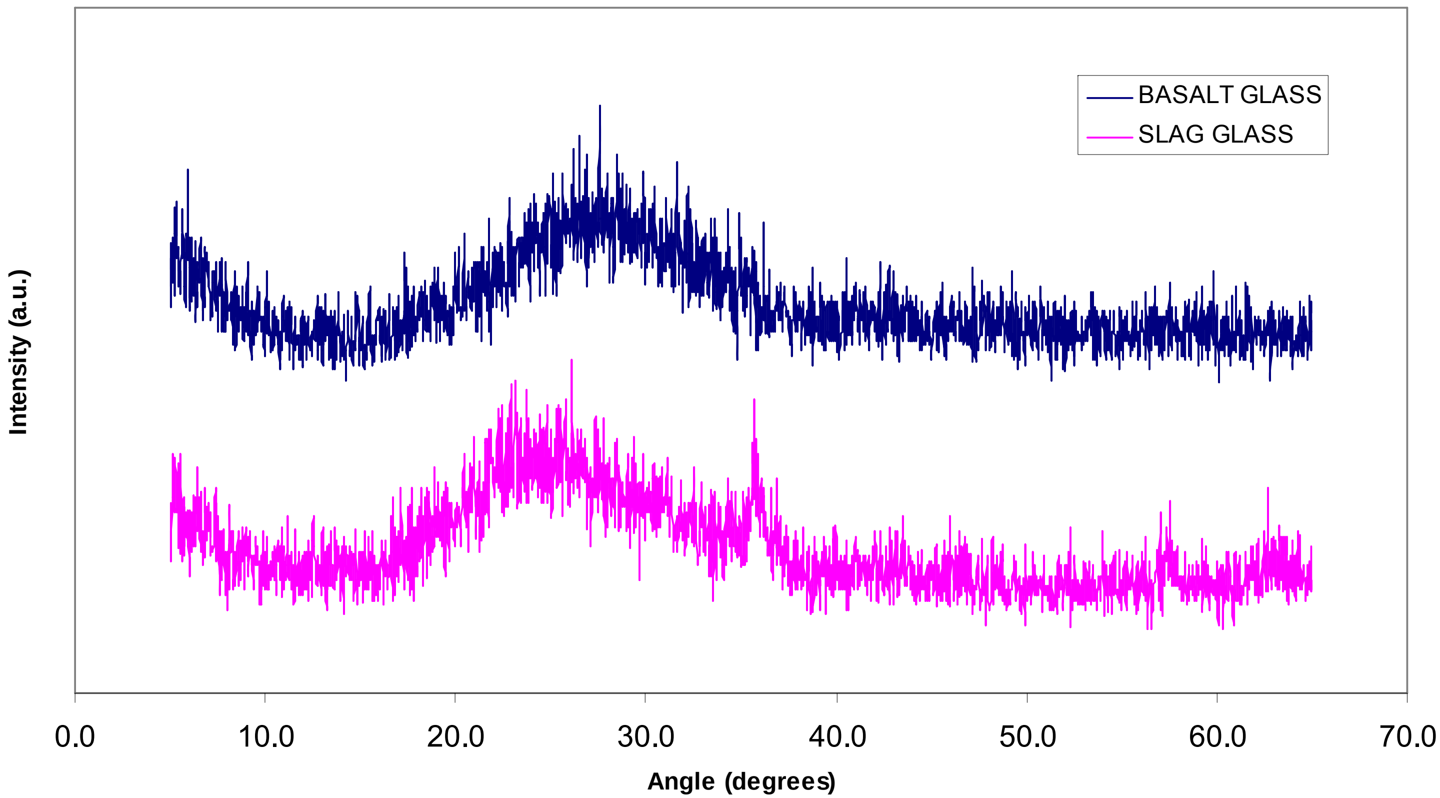
Slag, Glass Pieces and Glass Fibers



Composition in Atomic Percent

	Na	Fe	O	K	Ca	C	Mg	Si	Al	Cl	Zr
BASALT GLASS	0.6	0.4	51.5	0.9	6.5	13.7	3.5	13.9	8.3	0.4	0.3
SLAG GLASS	1.1	1.0	51.1	0.6	1.4	17.2	0.4	16.7	10.3		

X-ray Diffraction Results



Chemical Durability Testing in 2N NaOH at 70 C

	RAW SLAG	SLAG GLASS	SLAG GLASS FIBERS	BASALT GLASS	E-GLASS
after 0 hours	0.0%	0.0%	0.0%	0.0%	0.0%
after 3 hours	1.2%	0.3%	0.1%	0.1%	0.0%
after 15 hours	3.4%	0.7%	1.7%	0.3%	0.3%

Hardness Measurements

	SLAG GLASS	BASALT GLASS	FUSED SILICA	E-GLASS
Average Hardness (Vickers Units)	721	678	696	568
Average Hardness (GPa)	7.1	6.6	6.8	5.6

Frit for Inorganic Pigment Applications

- Evaluated vitrified fraction use as a frit (work done at Ferro Corporation)
- Vitrified material sample was grounded and then screen printed. The vitrified material did not adhere to the surface during screen printing.
- This could be due to the crystalline nature of this glass

Forming Glass Fibers

- The slag composition is very close to that of rockwool.
- The worldwide demand for rockwool is showing an increasing trend
- The decision was therefore made to explore the production of rockwool from frit
- In pursuing this route we learnt quite a bit about the intrinsic properties of the glass frit material

Forming Glass Fibers Contd

- The frit melts at 1600^{o} C/ Comparison E-glass melts at 1250^{o} C.

- Any rockwool manufacturing process utilizing this frit would be potentially more cost effective if the rockwool plant is integrated into the IGCC manufacturing process. In short the hot frit material would be fed directly into the rockwool manufacturing process, which would be a subsection within the IGCC manufacturing process.

Forming Glass Contd

- Significant foaming around 1250 C
- The foaming is due to the liberation of sulfur compounds

Forming Glass (Contd)

- The sulfur content raw slag was quantified
- 0.3% by sulfur on a weight basis as SO3
- Basalt glass contained 0.03% (weight percent)
- Slag glass contained <0.02% (weight percent)
- The melt temperature for basalt glass is 1250C
- Melt temperature for slag glass is 1600c

Forming Glass (Contd)

- Pull glass fibers from the melt (molten slag)
- Silica rod touched to the surface/ pulled vertically
- Fibers pulled were 100 (micro) m to 2mm
- Fibers showed roughness which is due to the crystalline nature of this glass as supported by x-ray diffraction

Composition in Atomic Percent

- XPS results showing the composition of the basalt and slag glasses in atomic percent. The slag is more refractory because it has more silica and alumina, and less alkali (K, Ca, and Mg) than the basalt glass

Composition in Atomic Percent

	Na	Fe	O	K	Ca	C	Mg	Si	Al	Cl	Zr
BASALT GLASS	0.6	0.4	51.5	0.9	6.5	13.7	3.5	13.9	8.3	0.4	0.3
SLAG GLASS	1.1	1.0	51.1	0.6	1.4	17.2	0.4	16.7	10.3		

Chemical Durability

- Chemical durability results show that the raw slag lost 3.4% by weight and the slag glass fibers lost 1.7% by weight after 15 hours in 2N NaOH.

- Slag glass fibers are more chemically durable than the raw slag

Discoveries Made/ Forming Glass

The foaming nature and high fraction of metals contained within the IGCC slag material could be exploited to create foam or microspheres. Either of these could yield (through mechanical crushing) thin, curved "shells" which may act as an airborne obscurant of electromagnetic radiation and/or heat. The microspheres, themselves, could also prove useful as low-density-filler for paints, plastics and powder coatings, or for high temperature fluidized bed media.

Discoveries Made/ Forming Glass Controlled Foaming

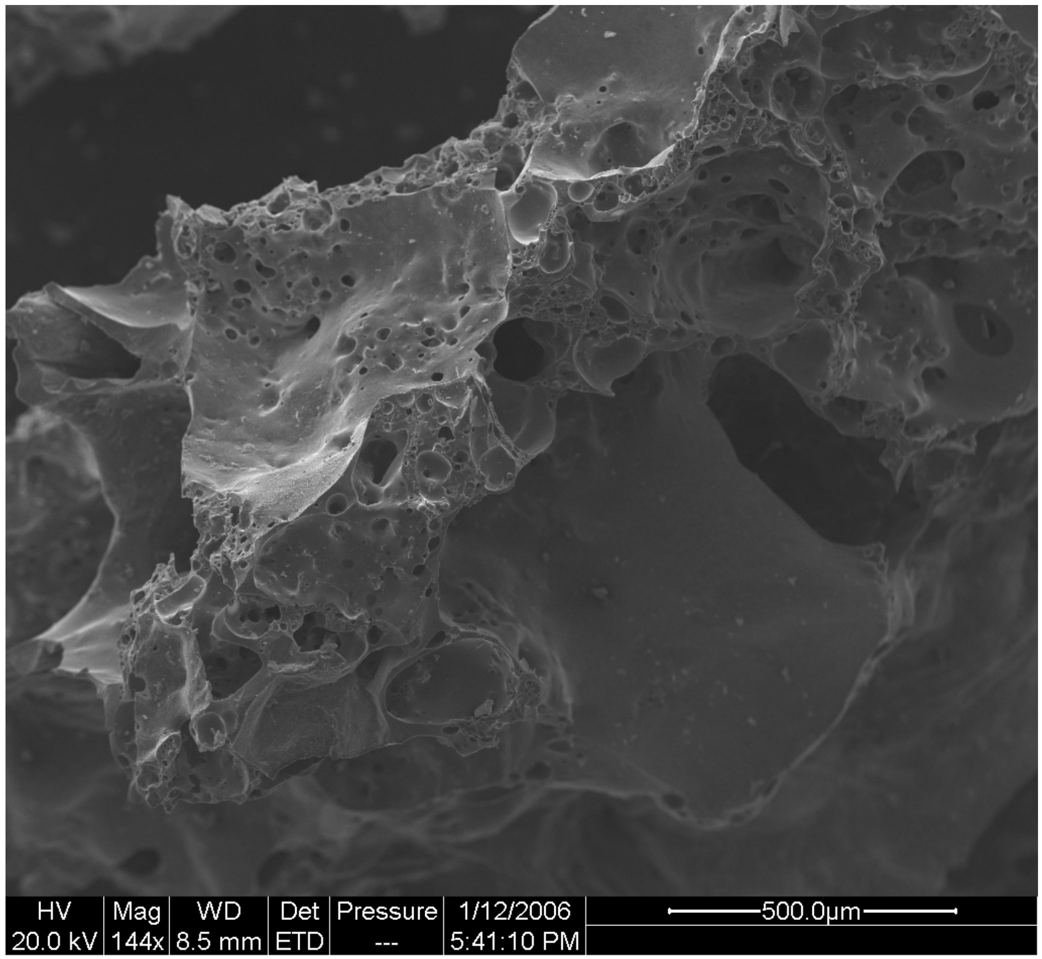
- First objective was to produce a foamed material of large cells with thin walls.
- The foamed structure was then crushed to produce “ear shaped cells” called orechietti. These would serve as the obscurant material.
- Several different foaming agents were evaluated. The material which resulted in optimized foaming was silicon carbide (SiC).

Discoveries Made/ Forming Glass Controlled Foaming

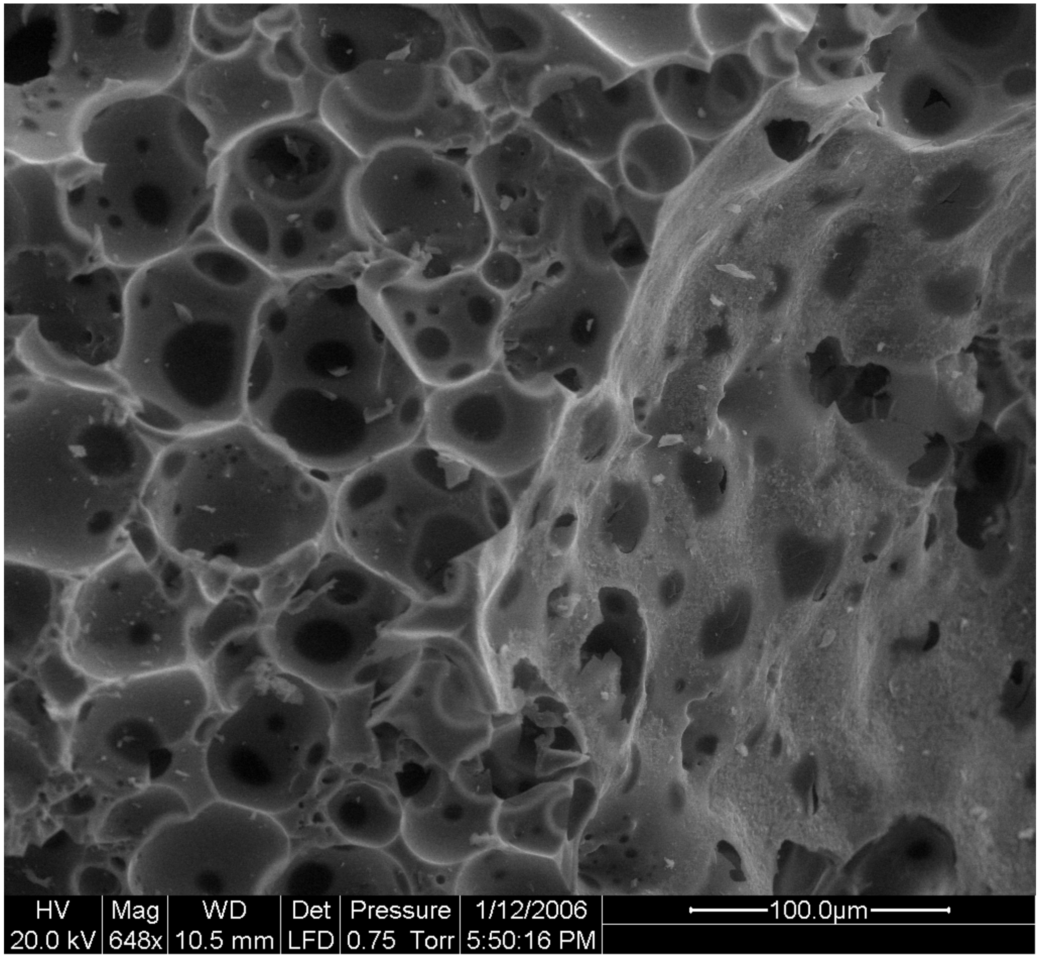
Experimental Conditions:

- 90 wt % slag (<180uM)/ 10 wt % SiC (600 mesh, 16 Um)
- Heated to 1200^{o} C/ Held for 45 minutes
- FEI Quanta 200 ESEM was used for taking the scans
- Wall thickness relatively uniform at 10uM

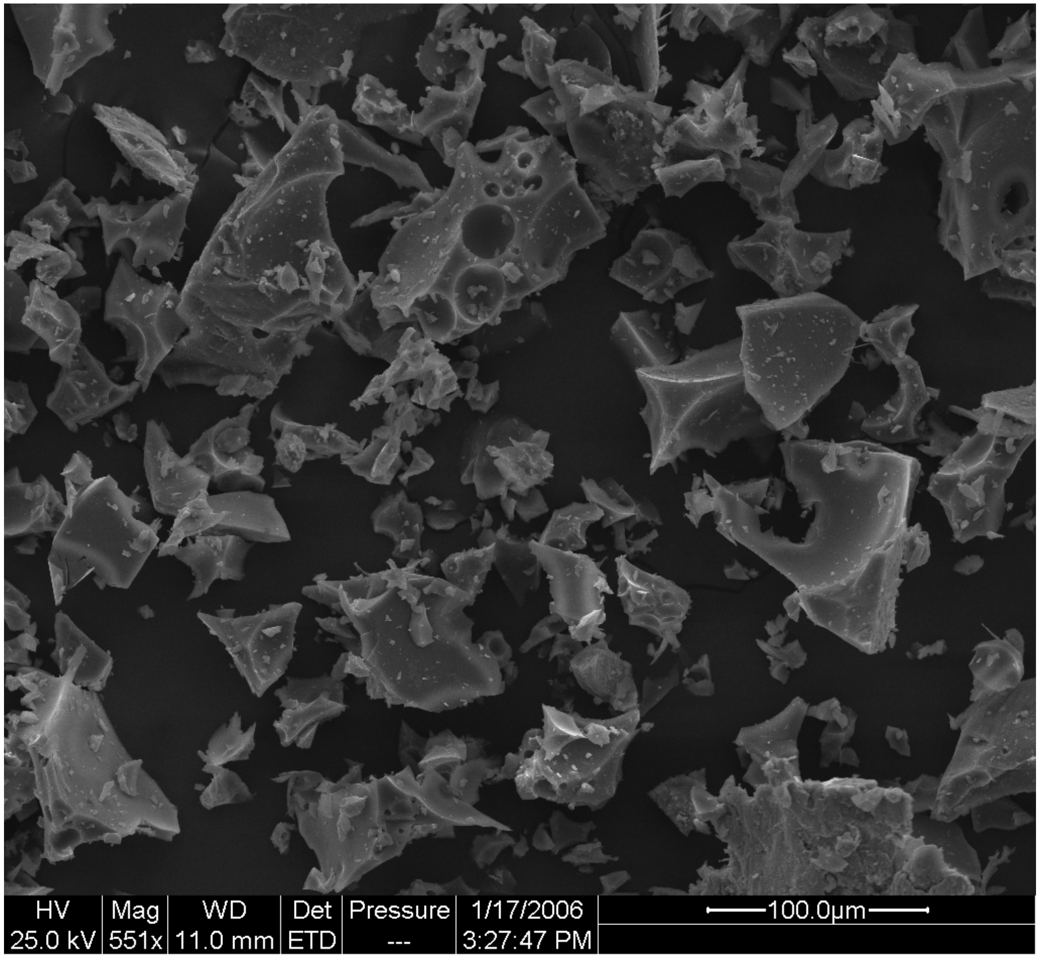
Scan of Foamed Shell



Scan Showing the Uniform Distribution of Cells in the Foam Matrix



Crushed Foam Glass



Glass Microspheres

While the surfaces created by foaming the slag material were curved and appropriate for obscuration, it was thought that a more uniform controlled curvature might be possible with glass microspheres.

Discoveries Made/ Forming Glass

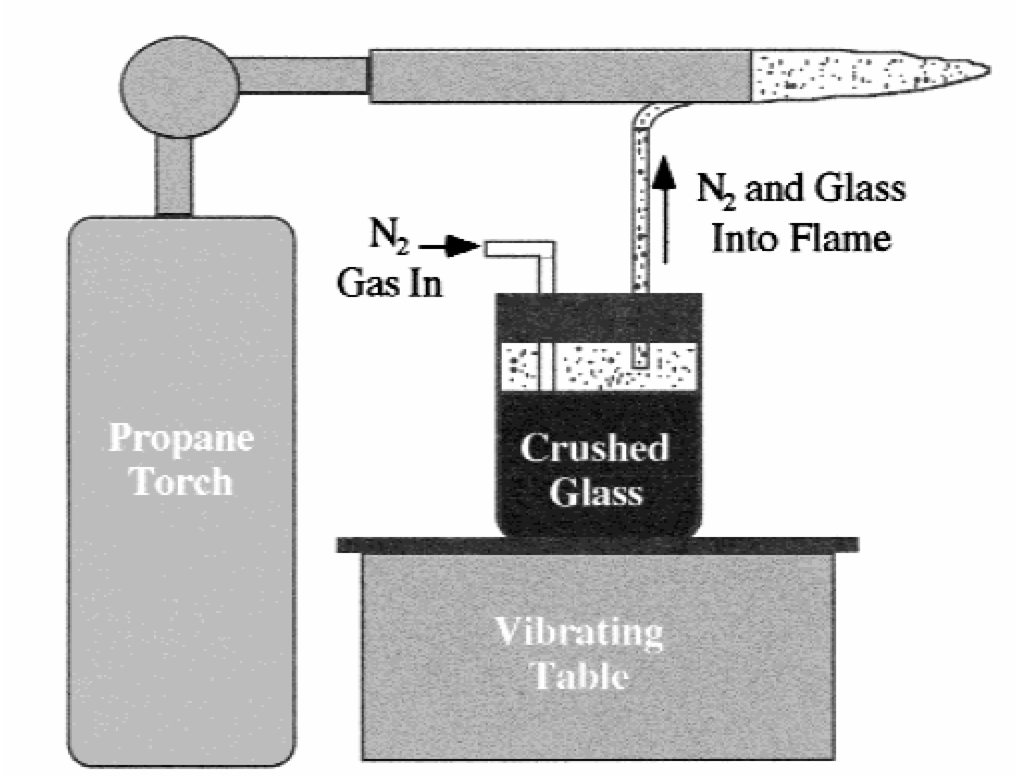
- When the aggregates are crushed and then pumped into a flame we can make micro-spherical particles.

- Potential uses are as follows:

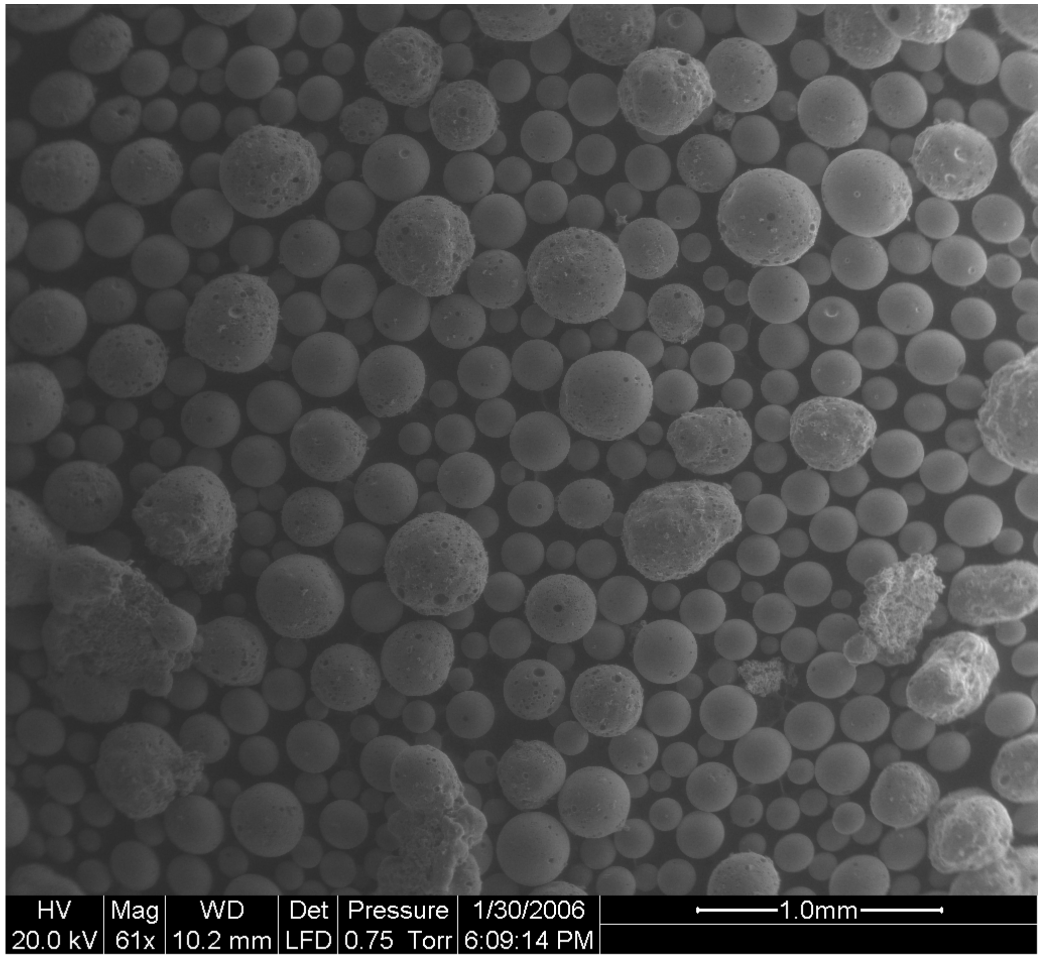
  Additives in concrete and cement

  Additives in plastics, paints, powder coating or high temperature fluidized bed media

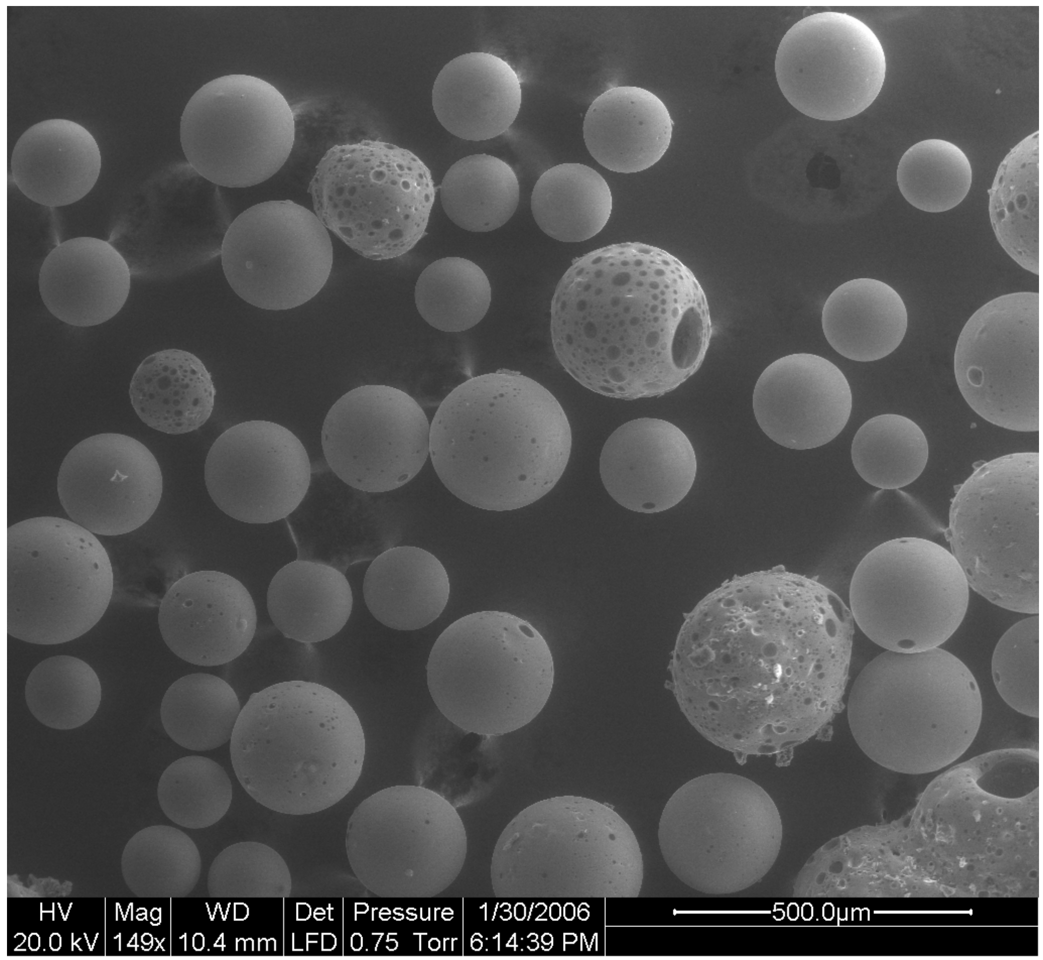
Schematic of the apparatus designed by Conzone for preparing glass microspheres.



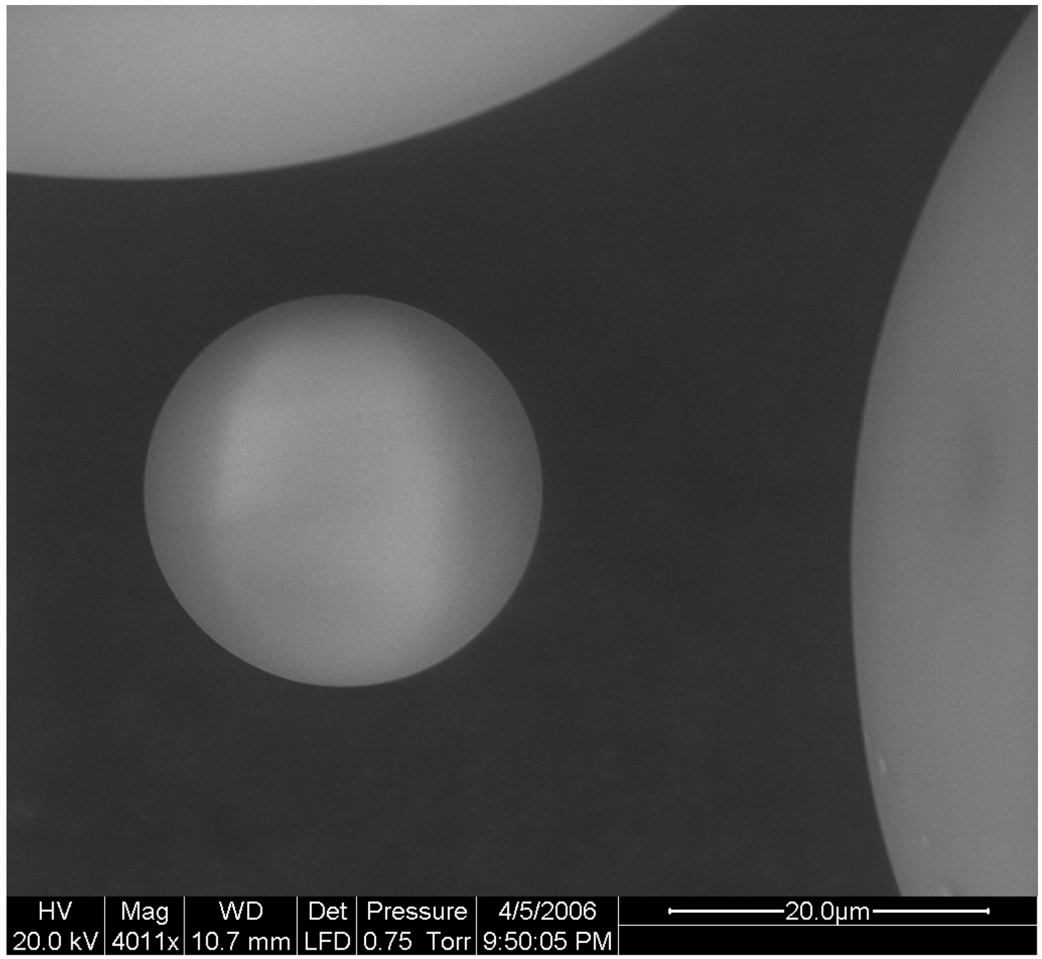
ESEM images of slag spheres created in an oxy-propane flame. The starting frit passed a 400 mesh (<38μm) sieve. The resultant particles range between 50 and 300μm in diameter, showing that the frit must be agglomerating as it is dropped into the flame.



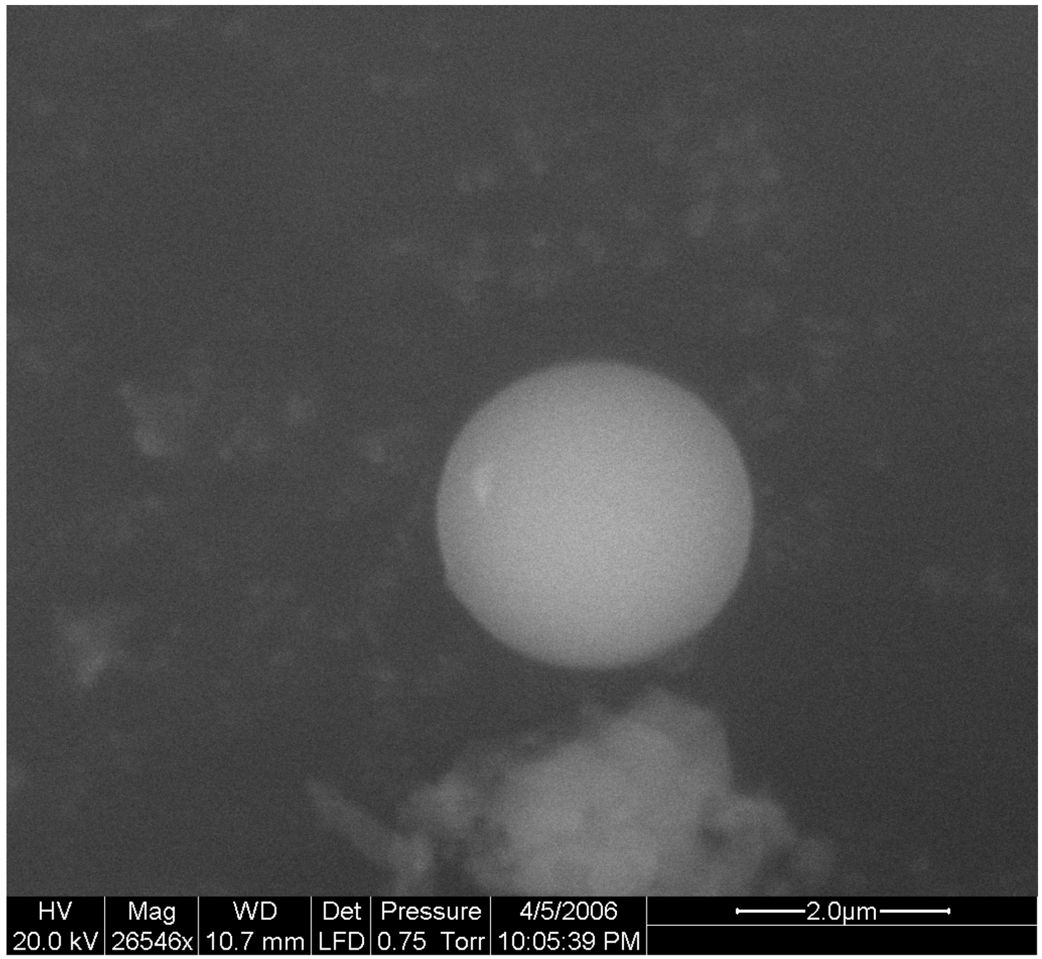
Microspheres at greater magnification



ESEM images of the smallest slag spheres created by this process.



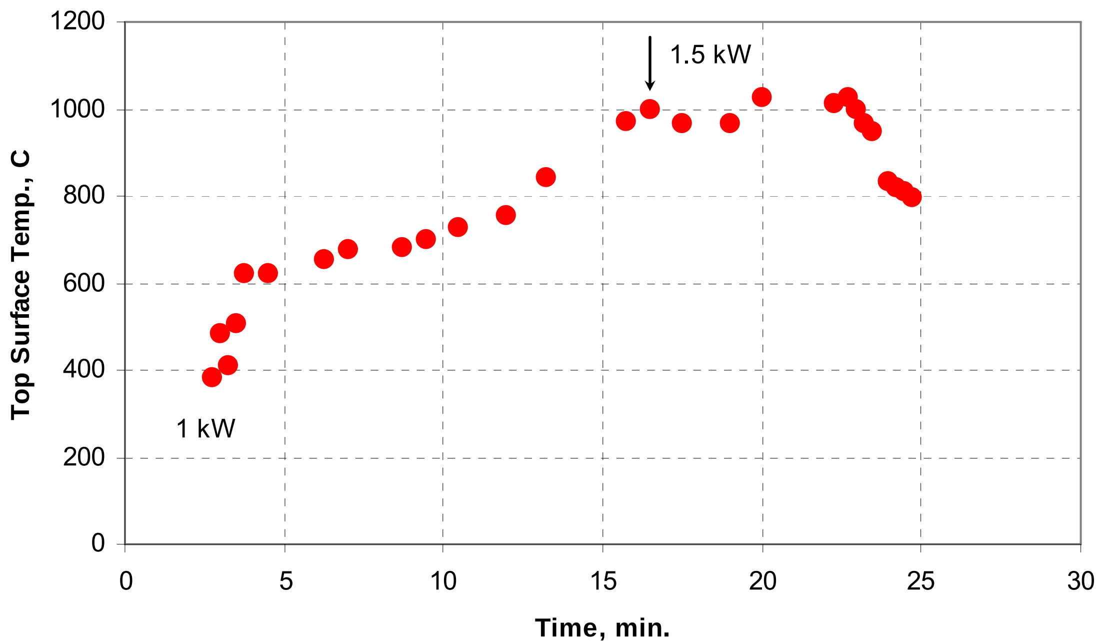
ESEM images of the smallest slag spheres created by this process.



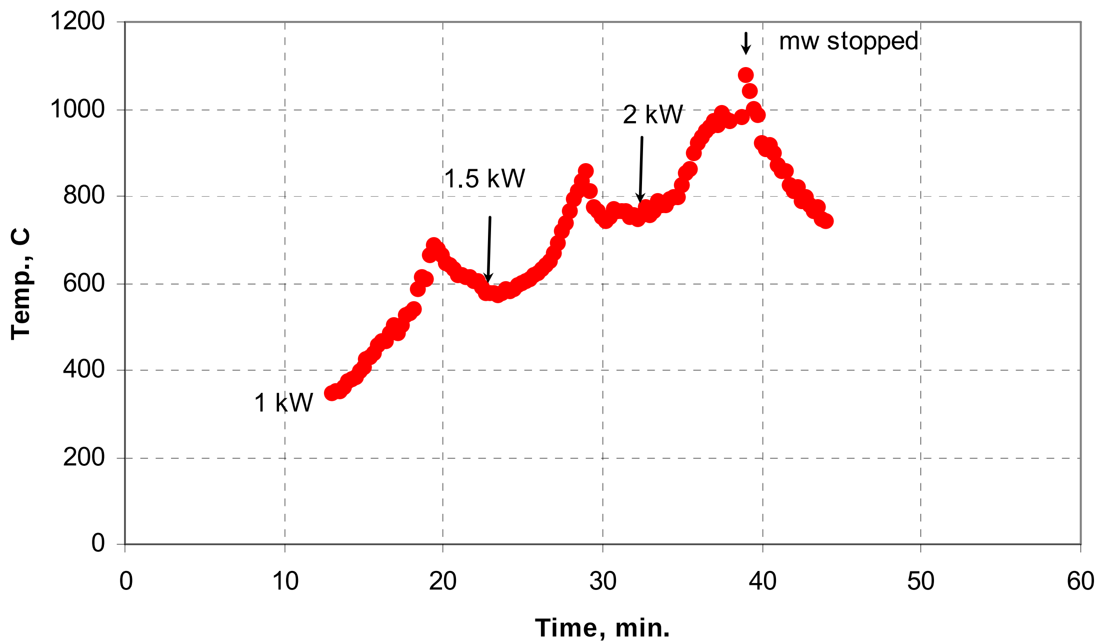
Other Significant Discovery: Microwave Heating of Slag

- Microwave heating was explored to determine if microwave melting of the frit could be more efficient.
- The presence of Fe in the glass could facilitate microwave melting and so preliminary experiments were performed.
- Studies were performed with and without a susceptor

Microwave Heating with Susceptor



Microwave Melting in Vacuum without Susceptor



Sample Heated with a Susceptor at Atmospheric Conditions

Sample Melted/ Heated in Vacuum without Susceptor

Recommendations

- The project team believes that additional focused studies should be performed to develop materials from byproduct frit that represent new markets from medium to large volume utilization. The following materials represent our best thinking at the present time.

- Fireproof glazing materials for steel structures
- Obscurance materials for defense applications
- Substrate for solar and other heat collection systems
- Spray Insulation material for the building industry