Environmentally Safe, Large Volume Utilization Applications for Gasification Byproducts

Final Report

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Abstract

Samples of gasification by-products produced at Polk Station and Eastman Chemical were obtained and characterized. Bulk samples were prepared for utilization studies by screening at the appropriate size fractions where char and vitreous frit distinctly partitioned. Vitreous frit was concentrated in the +20 mesh fraction while char predominated in the -20+100 mesh fraction.

The vitreous frit component derived from each gasifier slag source was evaluated for use as a pozzolan and as aggregate. Pozzolan testing required grinding the frit to very fine sizes which required a minimum of 60 kwhr/ton. Grinding studies showed that the energy requirement for grinding the Polk slag were slightly higher than for the Eastman slag. Fine-ground slag from both gasifiers showed pozzoalnic activity in mortar cube testing and met the ASTM C618 strength requirements after only 3 days. Pozzolanic activity was further examined using British Standard 196-5, and results suggest that the Polk slag was more reactive than the Eastman slag. Neither aggregate showed significant potential for undergoing alkali-silica reactions when used as concrete aggregate with ASTM test method 1260.

Testing was conducted to evaluate the use of the frit product as a component of cement kiln feed. The clinker produced was comprised primarily of the desirable components Ca_3SiO_5 and Ca_2SiO_4 after raw ingredient proportions were adjusted to reduce the amount of free lime present in the clinker.

A mobile processing plant was designed to produce 100 tons of carbon from the Eastman slag to conduct evaluations for use as recycle fuel. The processing plant was mounted on a trailer and hauled to the site for use. Two product stockpiles were generated; the frit stockpile contained 5% LOI while the carbon stockpile contained 62% LOI. The products were used to conduct recycle fuel tests.

A processing plant was designed to separate the slag produced at Eastman into 3 usable products. The coarse frit has been shown to be suitable for use as clinker feed for producing Portland cement. The intermediate-size product is enriched in carbon (58-62% C) and may be used as recycle fuel either in the gasifier or in a PC boiler. The fines product contains 30-40% C and may also be used as a recycle gasifier fuel, as is presently done at TECO"s Polk Station, however, due to gasifier operating requirements for the production of syngas, this is not feasible at Eastman.

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Executive Summary

The use of coal gasification to produce power or chemicals and fuels will increase in the U.S. in the next few years, due to its inherent energy and environmental efficiencies. The rate of increase is unknown, but even under slow growth models, the amount of solid by-products from these technologies will rise from hundreds of thousands to millions of tons per year within the next decade. If the objective of "zero emissions" from this technology is to be realized, the utilization and environmental safety of the solid by-products from gasification technologies in large volume applications must be addressed and developed early.

Samples of gasification byproducts produced at Polk Station and Eastman Chemical were obtained and characterized. The by-product from Polk consisted of gasifier slag that had been processed to remove -20 mesh material for recycle fuel while at Eastman, both coarse and fine slag samples were collected. Following characterization, bulk samples were prepared by screening at the appropriate size fractions where char and vitreous frit distinctly partitioned. Vitreous frit was concentrated in the +20 mesh fraction while char predominated in the -20+100 mesh fraction. Bulk samples were prepared accordingly for use in utilization studies.

The vitreous frit component derived from each gasifier slag source was evaluated for use as a pozzolan and as aggregate. Pozzolan testing required grinding the frit to very fine sizes. The energy requirements to accomplish this were a minimum of 60 kwhr/ton. Grinding studies showed that the energy requirement for grinding the Polk slag were slightly higher than for the Eastman slag.

Both of the fine-ground slag samples showed pozzoalnic activity in mortar cube testing and met the ASTM C618 strength requirements after only 3 days. Pozzolanic activity was further examined using British Standard 196-5, a method that assesses the pozzolanicity by determining the uptake of calcium by hydrated cement. The results suggest that the Polk slag was more reactive than the Eastman slag.

Both slag samples were also evaluated for potential use as aggregates in concrete using ASTM test method 1260. Neither aggregate showed significant potential for undergoing alkali-silica reactions which could produce harmful internal expansion in concrete.

Testing was conducted to evaluate the use of the frit product as a component of cement kiln feed. The clinker produced was comprised primarily of the desirable components Ca_3SiO_5 and Ca_2SiO_4, however, the amount of free lime present was excessive. The raw ingredient proportions were adjusted in order to reduce the amount of free lime present in the clinker.

A processing plant was designed to produce 100 tons of carbon from the Eastman slag to conduct evaluations for use as recycle fuel. The processing plant was mounted on a trailer and hauled to the site for use. Two product stockpiles were generated; the frit stockpile contained 5% LOI while the carbon stockpile contained 62% LOI. The products were used to conduct recycle fuel tests.

A processing plant was designed to separate the slag produced at Eastman into 3 usable products. The coarse frit has been shown to be suitable for use as clinker feed for producing Portland cement. The intermediate-size product is enriched in carbon (58-62% C) and may be used as recycle fuel either in the gasifier or in a PC boiler. The fines product contains 30-40% C and may also be used as a recycle gasifier fuel, as is presently done at TECO"s Polk Station, however, due to gasifier operating requirements for the production of syngas, this is not feasible at Eastman.

Results and Discussion

       The results and discussion of progress made during this reporting period are summarized in this section which is organized by Task. For clarity, major accomplishments of each Task are highlighted and a narrative description of specific activities follows.

Task 1.0 Sample Collection and Characterization.

       Representative composite samples of gasification by-products were obtained from gasifier at Polk Station and characterized as a function of particle size to determine partitioning of carbon and ash. Previous evaluations of these substrates revealed that frit, carbon and ash particles partition into distinct particle size ranges. Each size fraction was thoroughly analyzed for proximate and ultimate analyses as well as major oxides.

       The Polk slag sample was wet sieved and screen fractions dried at 70^0C. Each size fraction was then dry-sieved to ensure a higher efficiency of separation. The results of the sieve analysis are shown in Table 1.1 along with a microscopic description of each size fraction. What is immediately apparent is that while the sample contained 9% LOI, which was primarily carbon, there was a sharp partitioning of the LOI at a screen opening of 20 mesh (841 µm). Slag finer than this size contains 45% to 64% LOI while the slag coarser than this size contains essentially no LOI or carbon. Also apparent is that the slag sample is coarse (83.7% +20 mesh), which was not unexpected, since the sample had already been processed at Polk Station. There are two distinct particle shapes as well; angular and round, with the round particles being concentrated in finer fractions and absent from the coarse fractions.

       A more detailed screen analysis was conducted on a larger feed sample (Table 1.2), and again, there was a distinct partitioning of the carbon (LOI) at a screen opening of 20 mesh. The round particles did not partition into any particular size fraction, however, they did show some possible correlation with LOI.

       A similar approach was followed for the size characterization of the Eastman slag samples. As shown in Table 1.3, the Eastman slag contained 23.63% LOI. As with the Polk slag, there was a distinct partitioning of the carbon in the -20+100 mesh size fraction. An important difference between the two substrates was that the Polk slag contained much lower LOI since it had already been processed to remove a substantial amount of the carbon-enriched fractions. Nevertheless, both samples showed enrichment of carbon in the -20+100 mesh size fractions; the 49.57% LOI for the Polk sample and 60.71% LOI for the Eastman sample.

       A more detailed size analysis was conducted on the Eastman sample to determine if there was any further enrichment in the carbon by size. The results (Table 1.4) show that the -40+50 mesh fraction contained the highest level of carbon (71.07% LOI), although the other size fractions were still quite high in carbon (44 to 66% LOI). These results were used to determine the appropriate classification sizes for the bulk samples that would be used in utilization studies.

Table 1.1. Initial Size Characterization of Polk Slag Sample.

Sieve	Weight (%)	LOI (%)	LOI dist (%)	Microscopic Description
+8	44.07	0.01	-	Mostly angular slag; no rounds
-8+20	39.60	2.24	9.80	Mostly angular slag; no rounds
-20+50	11.42	45.42	57.36	Mostly angular slag; burnt carbon, few rounds
-50+100	3.31	63.91	23.41	Abundant angular and round slag
-100	1.60	53.52	9.44	
Total	100.00	9.04	100.00	

Table 1.2. Sieve Analysis of Polk Slag Sample.

Sieve	Weight (%)	LOI (%)	LOI dist	Microscopic Description
+20	84.98	3.07	25.94	No rounds
-20+30	4.70	27.96	13.10	20% rounds
-30+40	3.47	52.26	18.03	40% rounds
-40+50	2.70	63.87	17.16	50% rounds
-50+60	1.44	66.80	9.58	55% rounds
-60+80	1.33	64.00	8.50	60% rounds
-80+100	0.38	61.28	2.34	40% rounds
-100	1.00	53.81	5.35	20% rounds
Total	100.00	10.04	100.00	

Table 1.3. Initial Size Characterization of Eastman Slag Sample.

Sieve	Weight (%)	LOI (%)	LOI dist (%)	Microscopic Description
+8	32.97	0.01	-	Mostly vitreous frit, angular slag to spherical
-8+20	19.92	0.48	0.40	Abundant vitreous frit, mostly angular; some rounds
-20+50	20.55	61.66	53.62	Abundant char, some angular frit, few rounds
-50+100	15.65	59.47	39.40	Abundant angular char, some spherical glass
-100	10.90	14.20	6.56	Abundant spherical glass and char
Total	100.00	23.63	100.00	

Table 1.4. Size Analysis of Carbon-Enriched Portion of Eastman Slag Sample.			
Sieve	**Weight (%)**	**LOI (%)**	**LOI dist (%)**
-20+30	20.17	44.57	15.54
-30+40	35.32	49.40	30.15
-40+50	39.68	71.07	48.76
-50	4.84	66.34	5.55
Total	100.00	57.84	100.00

Chemical analyses of the slag samples using X-Ray Fluorescence are summarized in Tables 1.5 and 1.6. These results are presented on as as-received, dry basis. When removing carbon from the various size fractions, there were no major differences in chemical composition between the size fractions.

A bulk magnetic analysis of both slag samples was also performed using a Davis Tube Magnetic Separator (DTMS). The results concluded that there was only a minor amount of magnetic material present within each sample (<0.5 %).

Table 1.5. Chemical Analysis of Polk Slag Size Fractions Using X-Ray Fluoresence .						
Sample ID	**+8 mesh**	**-8+20 mesh**	**-20+50 mesh**	**-50+100 mesh**	**-100 mesh**	**Total**
Weight %	44.07	39.6	11.42	3.31	1.6	100.00
% Ash	100.00	97.93	55.55	39.53	46.83	91.25
%SiO2	53.98	52.60	29.18	19.33	23.37	48.63
%Al2O3	19.40	19.08	10.83	6.61	7.92	17.58
%Fe2O3	10.84	10.65	5.97	3.90	6.14	9.81
%CaO	3.69	3.65	2.02	1.24	1.50	3.34
%MgO	1.05	1.04	0.57	0.36	0.44	0.95
%Na2O	2.40	2.34	1.29	0.84	0.93	2.16
%K2O	2.33	2.29	1.30	0.84	1.02	2.11
%P2O5	0.66	0.65	0.39	0.25	0.34	0.60
%TiO2	0.99	0.97	0.56	0.36	0.42	0.90
%SO3	0.65	0.58	0.59	0.47	0.84	0.60
% LOI	0.10	2.24	45.42	63.91	53.52	9.09

Table 1.6. Chemical Analysis of Eastman Slag Size Fractions Using X-Ray Fluorescence.						
Sample ID	+8 mesh	-8+20 mesh	-20+50 mesh	-50+100 mesh	-100 mesh	Total
Wt (%)	32.97	19.92	20.55	15.65	10.90	100.00
% Ash	100.00	99.43	38.25	40.49	85.09	76.25
%SiO2	38.41	20.16	14.67	15.45	28.21	25.19
%Al2O3	20.29	10.68	7.93	8.37	18.31	13.75
%Fe2O3	27.91	14.65	10.77	11.53	34.67	19.92
%CaO	2.03	1.07	0.77	0.77	2.44	1.43
%MgO	0.95	0.5	0.37	0.39	0.92	0.65
%Na2O	0.32	0.17	0.11	0.11	0.28	0.21
%K2O	2.56	1.35	0.99	1.05	2.24	1.73
%P2O5	0.1	0.05	0.05	0.05	0.13	0.07
%TiO2	1.34	0.7	0.54	0.58	1.33	0.93
%SO3	1.71	0.78	0.82	0.62	2.6	1.27
LOI	0.10	0.48	61.66	59.47	14.20	23.65

The slag removal cycle from the gasifier at Eastman consists of periodically removing slag through a lock hopper into a quench tank. The coarse quenched slag is removed from the quench tank by a drag conveyor while fine slag is decanted through an overflow pipe where it is flocculated and filtered on vacuum drum filters. The analyses of the Eastman slag discussed thus far have been conducted on the coarse slag. A separate bulk sample of the fine slag (filter cake) was also collected for analysis. The filter cake sample contained 60.9% moisture; the size analysis is shown in Table 1.7. The +100 mesh portion of the filter cake was slightly higher in LOI than the same size fraction of the Eastman coarse slag while the LOI of the -100+200 mesh fraction of both samples were essentially the same. The -200 mesh fraction was predominantly ash with only 16% LOI.

Table 1.7. Size Analysis of Eastman Fine Slag Sample.			
Sieve	Weight (%)	LOI (%)	LOI Dist. (%)
+100	30.09	78.78	52.4
-100+200	18.02	61.36	19.3
-200	45.89	16.11	28.3
Total	100.00	36.55	100.00

Task 2.0 Composite Sample Preparation and Characterization.

A bulk sample of the Polk slag was prepared by dry screening at 20 mesh. The bulk sample contained 1.3% LOI and was utilized in Task 3. Similarly, a bulk sample of the Eastman coarse slag was also prepared by dry screening at 20 and 100 mesh. A total of 225 lbs of +20 mesh, 172 lbs of -20+100 mesh and 21 lbs of -100 mesh were recovered and was used in Task 3.

An additional sample of Eastman slag was collected on 14 March 2006. The original sample was collected on 1 February 2005 from the drag conveyor of the Eastman gasifier. There was some concern that the sample taken from the drag conveyor might have been biased since it was not possible to sample the conveyor during the first few minutes of each dumping cycle due to elevated CO concentrations. For this reason, the second sample was taken at the Eastman landfill site. An entire 20 ton slag truck sample was dumped in the middle of the landfill so that a random 1000 lb sample could be collected. A larger sample was collected to provide a higher level of confidence in the size distribution and to provide a sufficient quantity of frit to conduct concrete testing. Additionally, it was necessary to verify that the screen size where carbon and frit components partition had not changed. This determination was necessary for the completion of Task 5.

The entire 1000 lb sample (Sample ID 060201) was thoroughly mixed and a representative sub-sample was obtained and subjected to a wet screen analysis. A comparison of the size analyses of both samples is shown in Figure 2.1. There was essentially no change in the size distribution of the frit (+20 mesh) from both fractions. The original sample did a contain higher proportion of -20+50 mesh solids and correspondingly, less -50+100 mesh solids. Carbon analyses of the size fractions revealed that there was no substantial change in the size where the frit and carbon-enriched components partition. Thus, it was determined that the preparation of a bulk (100 ton) carbon sample would be completed by collecting the -20+100 mesh fraction.
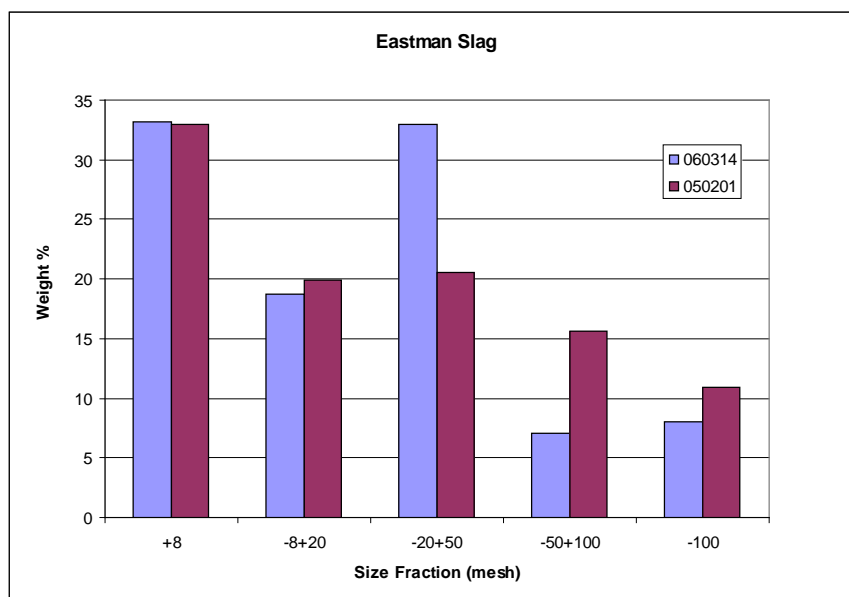
Figure 2.1. Comparison of Size Distributions of Eastman Slag Samples.

The entire 1000 lb. sample was oven dried and sized to recover the +20 mesh frit, which was used in concrete testing. Based on the size distribution of this material and results from pozzolanicity testing reported previously, it was expected that this component of the slag may be useful as an intermediate-size aggregate in concrete. Although this was not a specific task in the original Work Plan, concrete testing was conducted to verify this potential application. The entire +20 mesh size fraction was thoroughly mixed and washed in a concrete mixer to remove any residual carbon and the entire washed sample was again dried, re-screened and riffled to obtain a representative portion. The size analysis is shown in Figure 2.2 along with the carbon analyses for each size fraction.
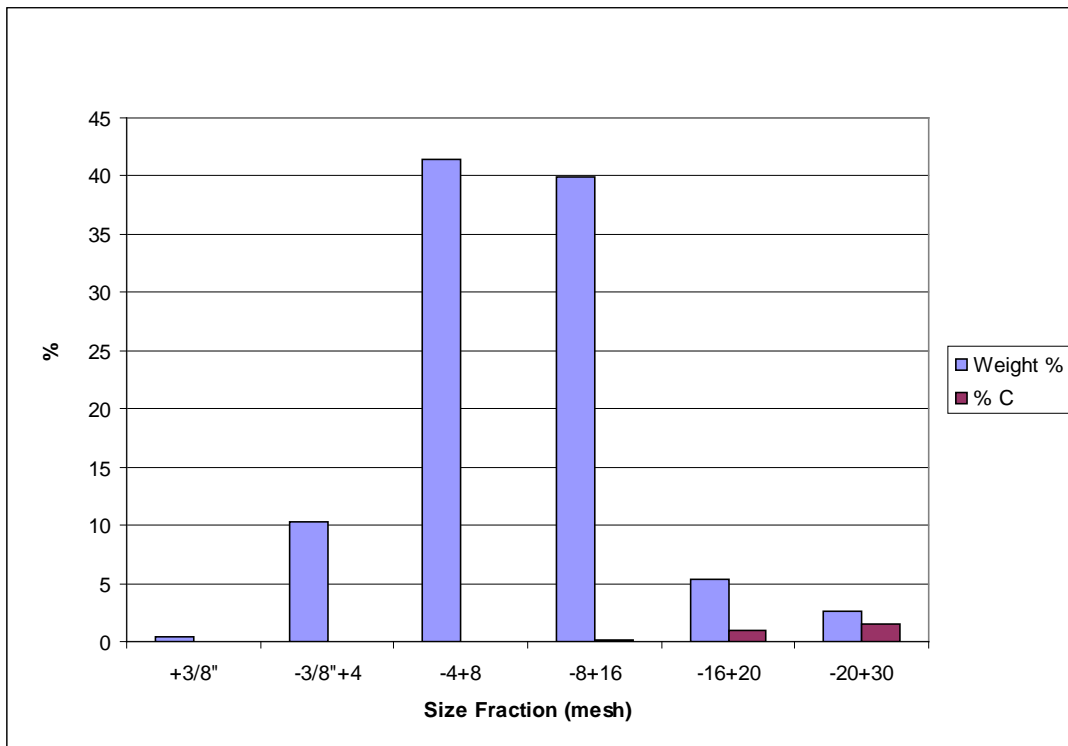
Figure 2.2. Size Distribution of Washed Eastman Frit.

.**Task 3.0 Lab-Scale Product Utilization Evaluation**.

Grinding Studies
The bulk slag or frit product from the Polk and Eastman samples prepared in Task 2 were evaluated for potential use as pozzolan. A representative portion of the bulk sample was riffled, crushed and ground to a size distribution suitable for evaluation studies which include mortar flow and compressive strength testing. In order to prepare the frit for fine grinding, the frit was dry crushed to -16 mesh using a hammer mill and disc pulverizer. The ground frit was then thoroughly mixed and representative portions were riffled to obtain samples for fine grinding studies.

Fine grinding was conduced using a Szegvari Batch Attritor Mill, which is a variable speed, stirred ball mill (see Figure 3.1). The grinding chamber was charged with carbon steel grinding media (4.5 mm diameter) and the appropriate amounts of ground frit and water. The slurry was agitated at the appropriate speed (200 rpm) and torque measurements were continuously recorded. A small aliquot of ground slurry was withdrawn from the base of the grinding chamber at various time intervals. The particle size distributions of these aliquots were later determined using laser diffraction. Incremental energy consumption was calculated for specific time intervals using the formula:

$$E = 3.6228 \times 10^{-6} \ T\omega t/M$$

Where T = shaft torque (in.lbs)
  Ω = shaft rotation (rpm)
  T = time in (seconds), and
  M = mass of feed (kg).

The results of initial grinding tests on the Polk frit are shown in Figure 3.2, which shows that higher feed solids (33% to 60%) provided similar size reduction for a given energy input. At these feed solids concentrations, reducing the average particle size of the feed to 25 µm required an energy consumption of approximately 50 kwhr/ton. Much higher energy consumption was required to reduce the average particle size further. At low feed solids (20%), energy consumption was much higher. This illustrates that most of the energy input into the mill was used for stirring the media.

Figure 3.1. Szegvari Batch Attritor Mill with Torque Meter.
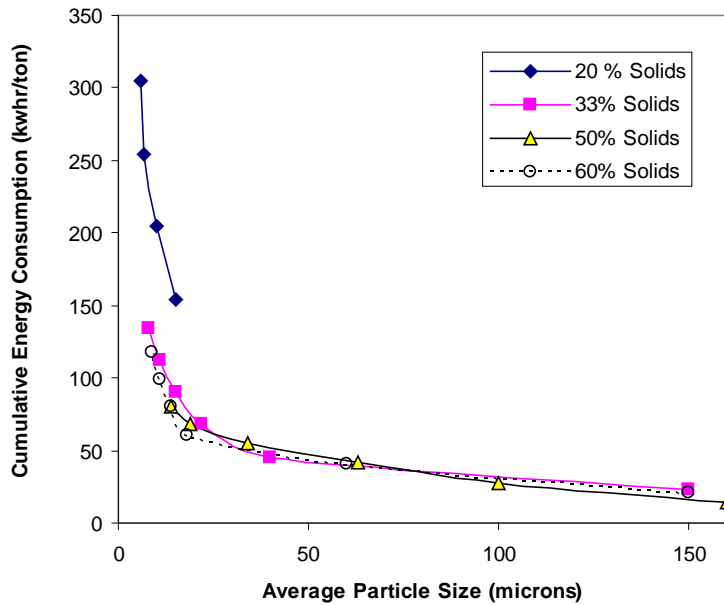
Figure 3.2. Effect of Feed Solids on Fine Grinding of Polk Frit.

There are several ways to express the extent of size reduction that occurred during grinding. One of the most common is the average particle size or d_{50} which is the size at which 50 wt % of the particles are finer and 50 wt% are coarser. A comparison of the d_{50} and cumulative energy consumption for Polk and Eastman frit is shown in Figure 3.3. In general, as the average particle size was reduced, energy consumption increased. Reducing the average particle size to 25 microns required approximately 60 kwhr/ton. Reducing the average particle below this size required significantly more grinding energy. It is apparent from this data that Polk material was harder than that from the Eastman gasifier. For example, to produce a d_{50} of 18 µm at 33% solids, the Eastman slag required 62 kwhr/ton, while the Polk slag required 81 kwhr/ton. Another way of interpreting the data is that for grinding at 33% solids, an energy consumption of 80 kwhr/ton provided a d_{50} of 11 µm for the Eastman slag and 18 µm for the Polk slag.
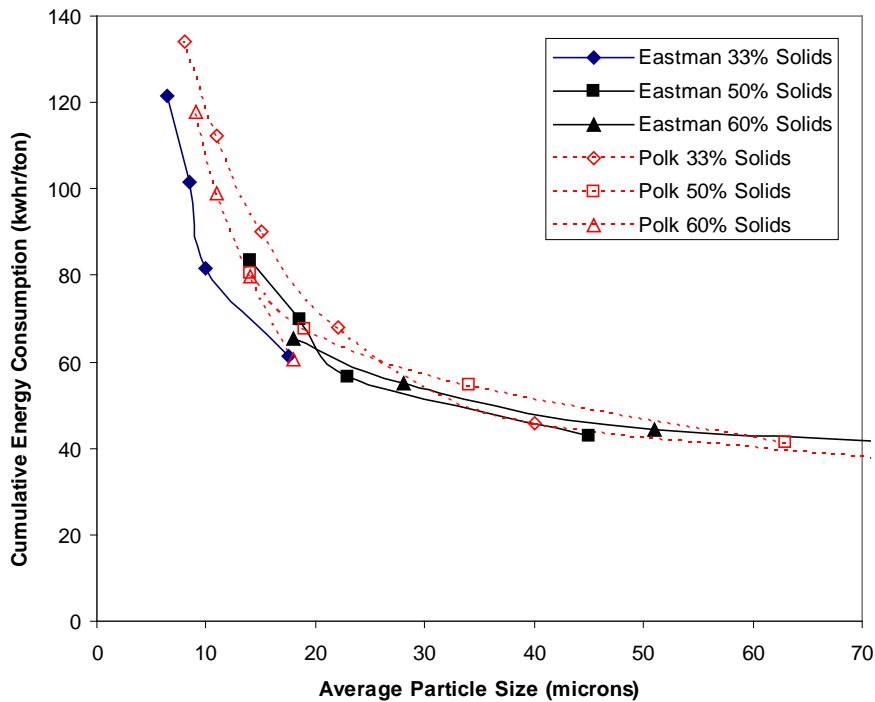
Figure 3.3. Average Particle Size vs. Energy Consumption for Polk and Eastman Frit.

When considering cement replacement as the intended use of the ground slag, it may be more convenient to express size reduction as a function of weight % finer than 325 mesh or 45 µm. ASTM size specification for coal combustion fly ash used for this purpose is a minimum of 66% passing 325 mesh. As shown in Figure 3.4, the minimum amount of grinding energy necessary to meet these size reduction requirements was 60 kwhr/ton; finer grinding required additional energy. As with considering d_{50} as a measure of size reduction, when considering the amount passing 325 mesh, the Polk slag appeared to require more energy than the Eastman slag, although this was not always the case. At 50% solids, the Eastman slag appeared to be harder, although the differences were minor.

Perhaps the most meaningful means of expressing size reduction for use in cementitious applications is the amount of ultra-fine (-10 µm) material generated by grinding. A size range of -10 µm particles was selected because this is the size range that accounts for most of the surface area available for cementitious reactions. As shown in Figure 3.5, an energy consumption of 60 kwhr/ton generated 20 to 25% -10 µm particles for the Polk slag and 30 to 40% for the Eastman slag. It is apparent from this data that the Polk slag is indeed harder than the Eastman slag, at least when considering the amount of energy required to grind each substrate to a very fine size.
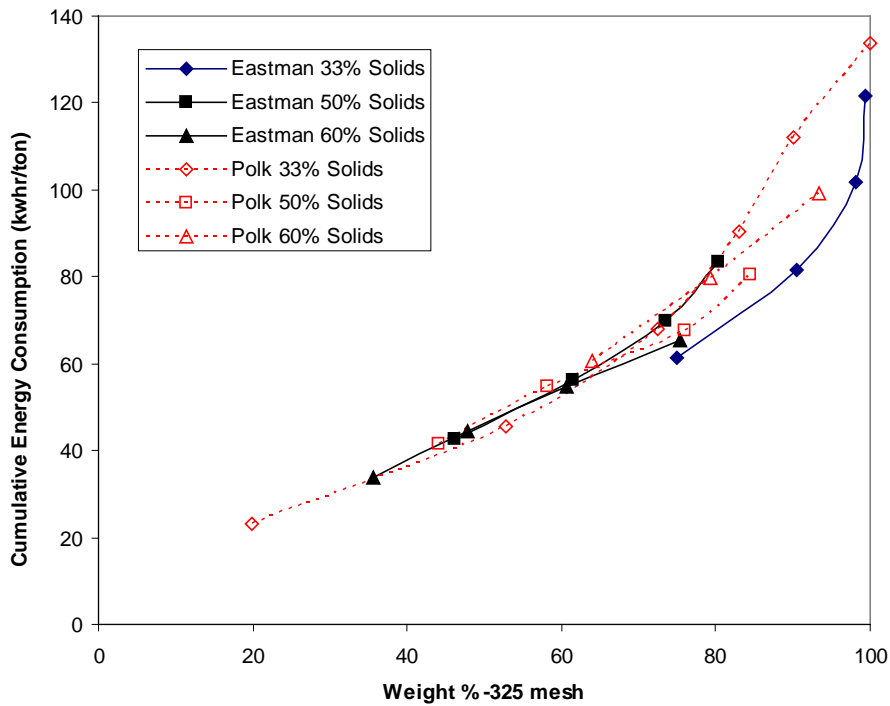
Figure 3.4. Weight % -325 Mesh vs. Energy Consumption for Polk and Eastman Frit.
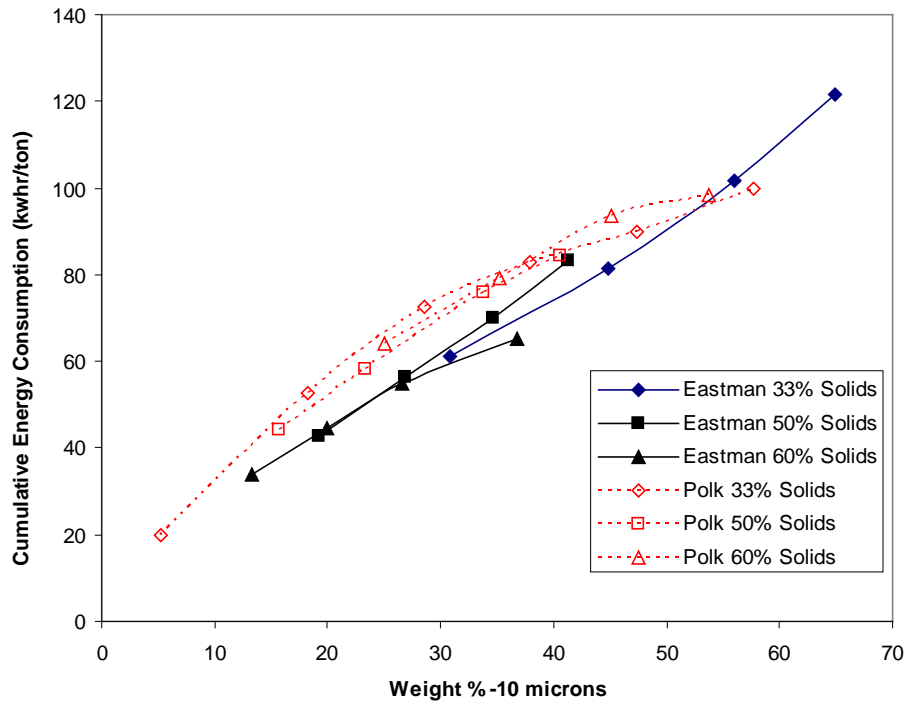
Figure 3.5. Weight % -10µm vs. Energy Consumption for Polk and Eastman Frit.

Mortar Preparation

The vitreous frit that was processed in the Attritor mill was examined for its potential use as a mineral admixture in Portland-cement concrete. Mortar batches were prepared in accordance with ASTM C 305, using ordinary Portland cement, ground gasification slag, de-ionized water and standard sand. Both the Eastman and Polk batches utilized a 20% replacement of cement with ground gasification slag. The slag mortars were prepared at an equivalent flow (i.e. workability) as an ASTM standard mortar following ASTM C 109, which had a water:cementitous (w:cm) ratio of 0.485.

Unconfined Compressive Strength of Mortar

Mortar samples were prepared for unconfined compressive strength (UCS) testing by casting into cube molds (5.1cm x 5.1cm x 5.1cm) in accordance with ASTM C 109. The addition of the gasification slag to the mix did not reduce the water demand. As seen in Table 3.1, the mortar flow (i.e. workability) for the slag mixes was between 89% and 91%; which is within ±5% of the mortar flow of the control mix, as specified in ASTM C 109.

Table 3.1. Mortar Flow Data for Ground Eastman and Polk Slag.		
Sample	**D50**	**Mortar Flow (%)**
Control	20	91.9
Eastman	14	90.6
Polk	14	89.5

Unconfined compressive strength data were acquired after 3, 7, 28, 56, and 112 days of curing and is summarized in Table 3.2. The test results show that the UCS increases with increasing grind time, indicative of increasing slag reactivity with decreasing particle size. Table 3.2 shows that there was only a minimal strength gain between the 22.5' and 30' grind times. This small difference reflects the diminishing capability of grinding the slag in the ball mill, with the selected sizes of media. Results are shown graphically in Figures 3.6 and 3.7.
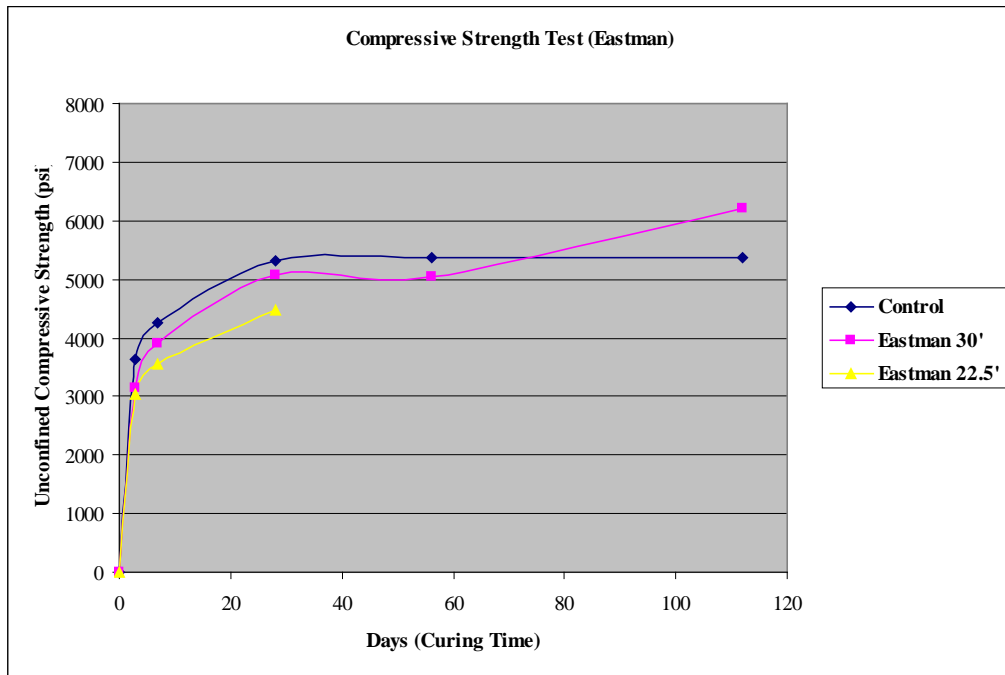
Figure 3.6. Unconfined Compressive Strength with Ground Eastman Slag.
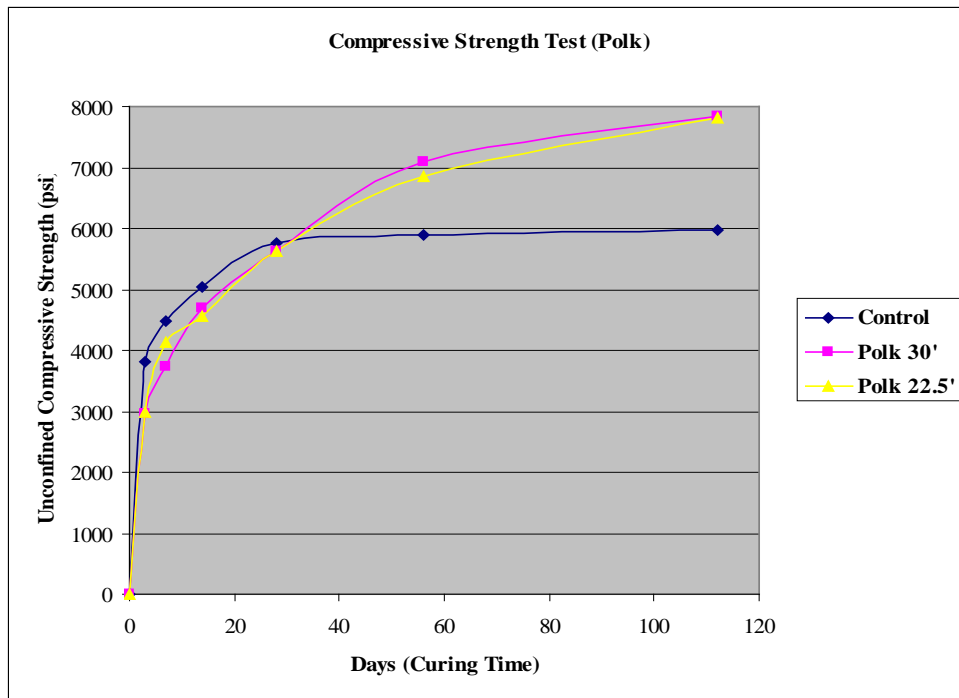
Figure 3.7. Unconfined Compressive Strength with Ground Polk Slag.

Figure 3.8 and Figure 3.9 show the progression of the UCS for the cubes with slag, as compared to the UCS for the control cubes, also known as the strength activity index. In accordance with ASTM C 618, the slag mortars were within 75% of control after only 3 days. The Polk slag surpassed control after approximately 28-days, whereas the Eastman slag required several months to achieve control strength. These results are similar to that obtained using Class F fly ash.

Table 3.2. Unconfined Compressive Strength of Mortar with Slag.						
Slag Used in Mortar	Grinding Time (min)	Unconfined Compressive Strength (PSI)				
		3-Day	7-Day	28-Day	56-Day	112-Day
Polk	15	3181	3436	4900	5904	6943
	22.5	2979	4127	5617	6844	7809
	30	2961	3723	5629	7092	7844
Eastman	22.5	3029	3556	4479	5437	6250
	30	3157	3917	5070	5031	6208
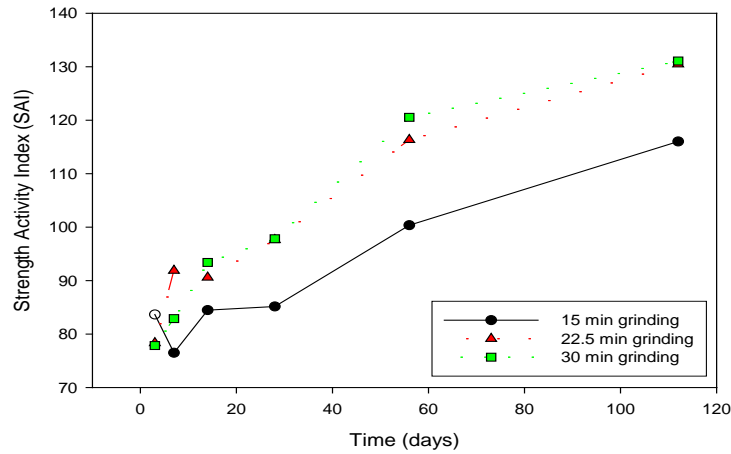
Figure 3.8. Strength Activity Index for Ground Polk Slag Mortar.
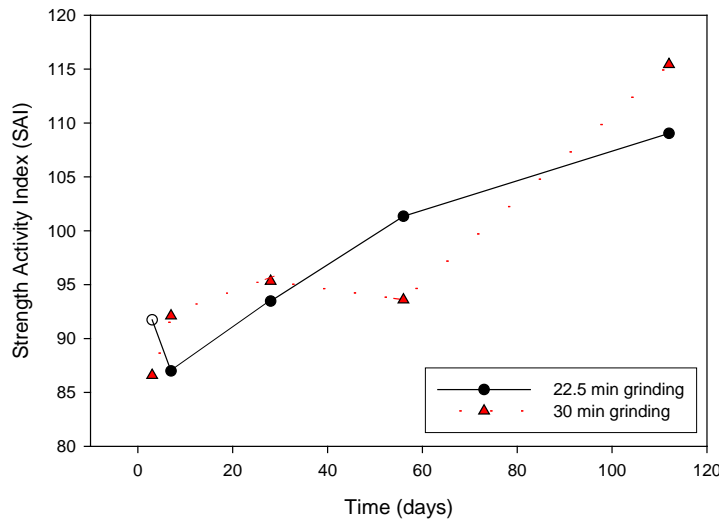
Figure 3.9. Strength Activity Index for Ground Eastman Slag Mortar.

Pozzolanicity Test

The finely-ground vitreous frit from both Eastman and Polk slags were examined following the British Standard 196-5 "Pozzolanicity test for Pozzolanic cements". This test method assesses the pozzolanicity by comparing the quantity of calcium hydroxide present in an aqueous solution in contact with the hydrated cement, after a fixed period of time, with the quantity of calcium hydroxide capable of saturating a solution of the same alkalinity. The test is considered positive if the concentration of calcium hydroxide in the solution is lower than the saturation concentration.

The data for Eastman and Polk are shown in Table 3.3. The results in Figure 3.10 show that the Polk samples satisfied the pozzolanicity test, illustrated by the points plotted below the curve of calcium oxide saturation. However, the Eastman samples did not satisfy the test. An additional test was performed to verify the results of Test 1; the results of the second test are shown in Figure 3.11. The data of Test 2 show improved repeatability, and exhibits Ca^{2+} values proportional to the Ca^{2+} values attained using an inductively coupled plasma-mass spectrometer (ICP-MS). The ICP-MS is an instrument used to determine trace elements in solution. Test 2 is believed to provide a more accurate representation of the pozzolanicity of the Polk and Eastman slags. Differences between the tests may have resulted from the variability of the Portland cement mixes.

Table 3.3. Pozzolanicity Data for Eastman and Polk Ground Vitreous Slags.				
	Sample	**Grind Time**	**OH⁻ (mmol/L)**	**Ca^{2+} (mmol/L)**
	Sand	**--**	53.85	11.37
Test 1	**Portland Cement**	**--**	59.14	9.96
	Eastman	**15'**	58.84	11.82
		22.5'	58.04	10.77
		30'	55.74	8.95
	Polk	**15'**	55.64	8.41
		22.5'	53.94	6.10
		30'	54.15	5.62
Test 2	**Portland Cement**	**--**	63.09	8.73
	Eastman	**15'**	53.69	8.79
		30'	54.29	5.33
	Polk	**15'**	48.33	7.99
		30'	53.59	5.82
ICP-MS (Test 2 samples)	**Portland Cement**	**--**	63.09	6.23
	Eastman	**15'**	53.69	5.87
		30'	54.29	4.46
	Polk	**15'**	48.33	5.38
		30'	53.59	3.81
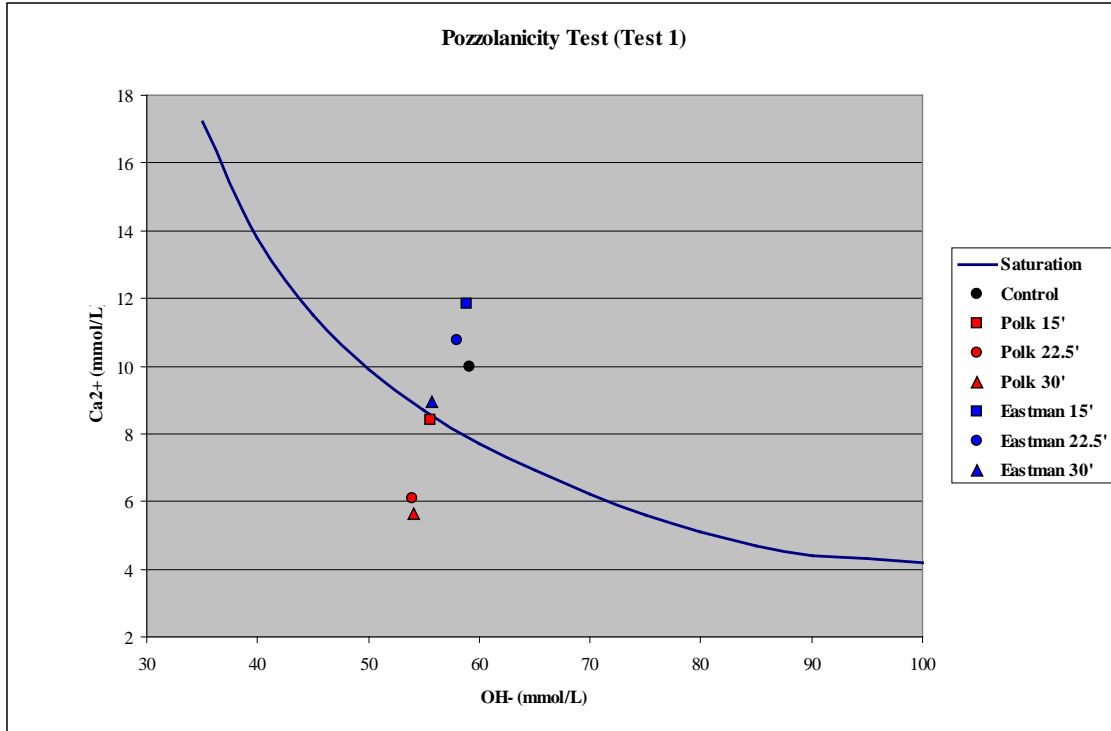
Figure 3.10. Pozzolanicity Data for Test 1.
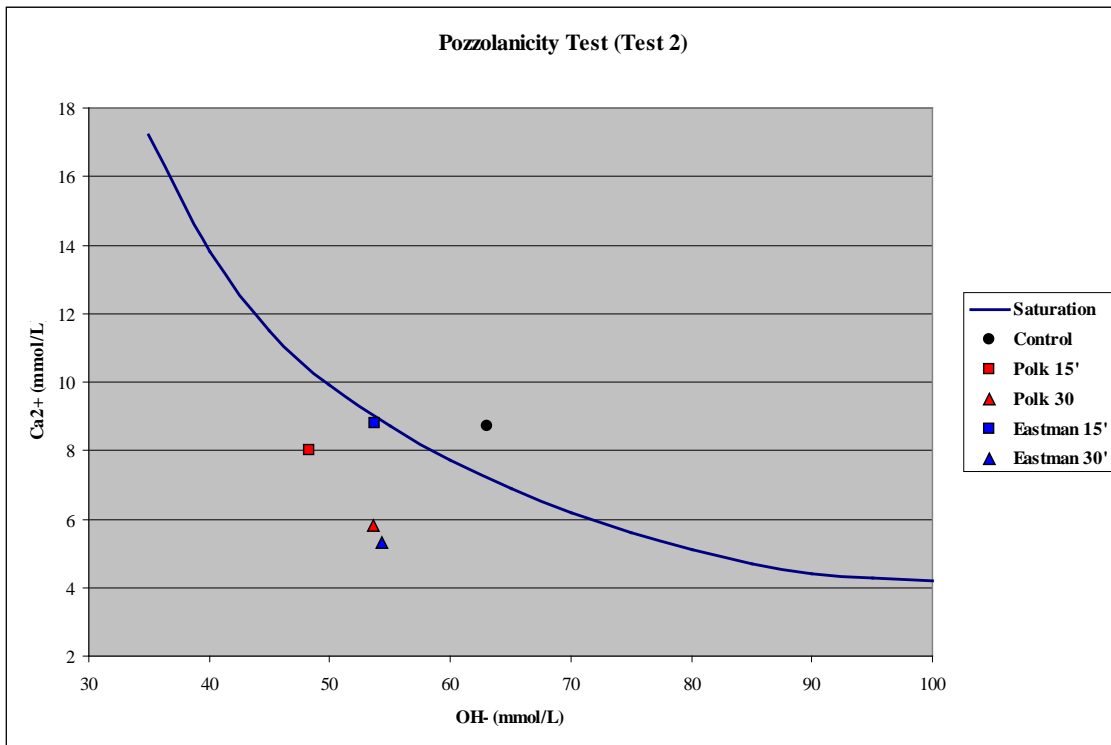
Figure 3.11. Pozzolanicity Data for Test 2.

Mortar Bar Expansion

Following ASTM test method C 1260, the vitreous frit was examined for its potential use as a fine aggregate in concrete. This test method provides a means of detecting the potential of an aggregate, intended for use in concrete, for undergoing the deleterious alkali-silica reaction, resulting in potentially harmful internal expansion. It may be especially useful for aggregates that react slowly or produce expansion late in the reaction. Figure 3.12 shows a plot of the percentage of expansion that the Eastman and Polk mortar bars have undergone. According to ASTM C 1260, expansions of less than 0.10% at 16 days after casting are indicative of satisfactory behavior in most cases. The Eastman mortar bars showed no signs of expansion after 14 days, with only a slight expansion of 0.01% after 21 days. The Polk mortar bars experienced similar expansions of 0.01% at 14 days, and 0.05% at 21 days. This concludes that neither the Eastman nor the Polk vitreous slags show signs of potential alkali reactivity. These data are consistent with those presented in the previous section, in that the Polk slag appears to be more reactive in Portland cement mortar.
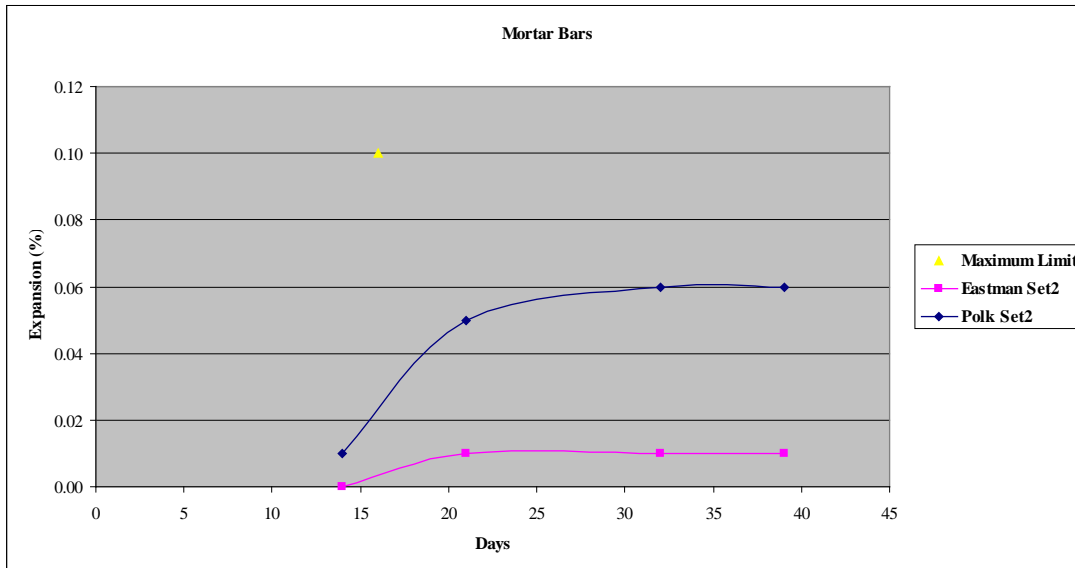
Figure 3.12. Potential Alkali Reactivity for Eastman and Polk Slag Aggregates.

Use of Slag as a Concrete Aggregate

During processing of the Eastman slag it was observed that the particle size gradation was similar to so-called "intermediate" aggregates commonly used in concrete. Intermediate aggregates are used to fill a gap in aggregate gradations that often occur between the 8 and 30 mesh (2.4 to 0.6 mm) sieve size, which is shown in Figure 3.13. Note that the Eastman slag is comprised largely of this size fraction. The coarse, intermediate and fine aggregate (sand) is then combined such that the percent retained on each sieve is not greater than 18% or less than 8%; this is represented by the dashed line in Figure 3.13. The concrete mix proportions are provided in Table 3.4, and were prepared at a constant water:cement ratio. Concrete cylinders (4 in diameter X 8 in length) were prepared according to ASTM C 192 and C 39 for testing of unconfined compressive strength (UCS) and ASTM C 1202 for rapid chloride permeability (RCP).
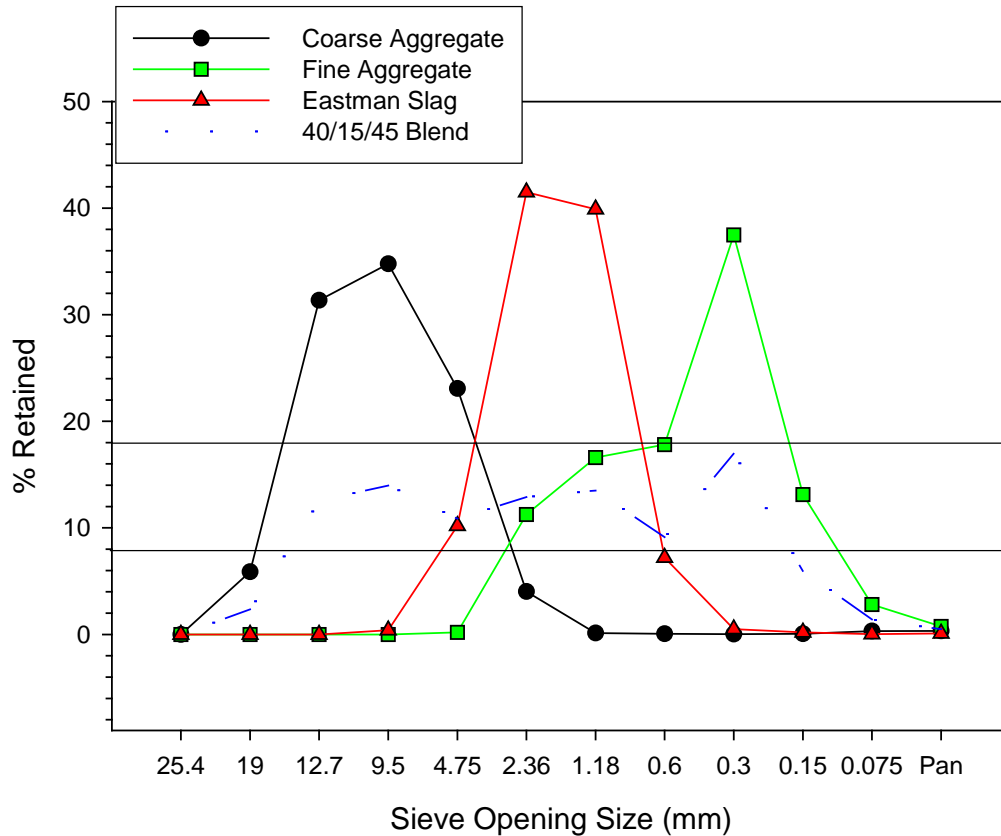
Figure 3.13. Concrete Aggregate Gradations.

Table 3. 4. Concrete Mix Proportions.			
Component	**Mix #1**	**Mix #2**	**Mix #3**
Portland Cement (kg)	9.8	9.7	9.8
Coarse Stone (kg)	24.9	22.0	30.6
Intermediate Stone (kg)	5.7	0.0	0.0
Eastman Slag (kg)	0.0	9.0	0.0
Fine Aggregate (kg)	19.9	19.7	19.9
Water (kg)	4.8	4.7	4.8
Slump (in)	3.5	2.0	3.25

Unconfined compressive strength data of the concrete cylinders are shown in Figure 3.14. The data indicate that the Eastman slag had similar strength as the concrete prepared without intermediate aggregates, whereas it was slightly weaker than concrete containing crushed limestone intermediate aggregate. The latter results may be caused by the low physical strength of the Eastman slag compared to crushed limestone.

The RCP testing results suggest that the permeability of the three concrete mixes was essentially the same although true permeability relationships are only inferred from RCP data (Table 3.5).

23
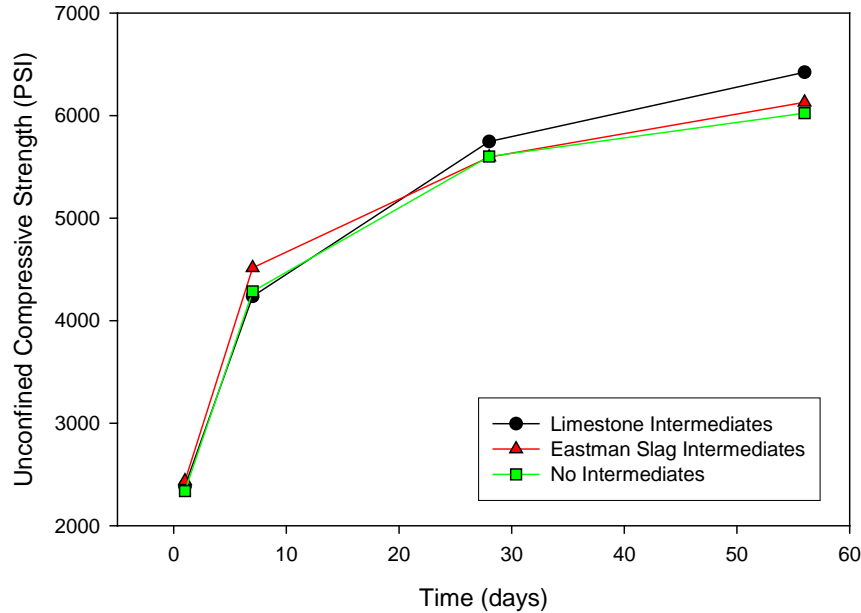
Figure 3.14. Unconfined Compressive Strength of Concrete Cylinders.

Table 3.5. Rapid Chloride Permeability of Concrete.	
Sample	**RCP (coulombs)**
Limestone Intermediates	3127
No Intermediates	2991
Eastman Slag Intermediates	3005

Task 4.0 Environmental Evaluation and Leaching Tests.

Gasification slag samples were tested using several leaching procedures; the results obtained with the Polk slag are shown in Table 4.1. In this evaluation, leaching was conducted on the slag using three different sample preparation techniques in distilled, deioinzed water; dry ground to -75 µm (liquid/solid ratio of 10.41), bulk sample at a similar liquid/solid ratio (10.71), bulk sample at more dilute liquid/solid ratio (1.41) and a duplicate or the dilute bulk sample. The pH of the post-filtered leachates ranged from 7.20 to 7.41.

Comparing the ground and bulk slag samples, the conductivity of the ground sample was higher (317 vs. 112 ohm/cm) while leachate concentrations of most parameters tested were either below detection limits or somewhat higher, with the exceptions of Ba, Li, Mo and Ni.

When leaching was conducted on the bulk sample under more dilute conditions (liquid/solid ratio 1.41), there was an increase in the following elements: Ca, Fe, K, Mg, Na, Cl, F, Ni as well as nitrates and sulfates.

The results of additional leaching tests using Toxic Characteristic Leaching Procedure (TCLP) are show in Table 4.2. The primary difference between the TCLP leachates of un-ground and ground Polk gasification slag were slight increases in the concentration of Ba (0.02 mg/l vs. 0.08 mg/l), Se (0.002 mg/l vs. 0.006 mg/l) and Cr (0.07 mg/l vs. 1.43 mg/l). Even when

the Polk slag was ground to -45 µm, leachates were well below the maximum concentration standards for all elements. In addition, leachate quality was below Drinking Water Standards for all elements tested, with the exception of Cr. Results obtained for the Eastman slag were essentially the same.

Table 4.1 Leaching Results for Polk Gasification Slag.

		Ground to -75 µm	Bulk	Bulk	Bulk	Blank
Method		D&D Water	D&D Water	D&D Water	D&D Water	D&D Water
Grams solids		40.5	40.5	250	250	-
Grams liquid		421.7	433.8	351.9	343.8	-
Liquid/solid		10.41	10.71	1.41	1.38	-
pH	post filter	7.41	7.24	7.23	7.20	-
Conductivity	ohm/cm	317	112	693	624	-
Parameter	Concentration					
Al	mg/l	<0.01	<0.01	<0.10	0.16	<0.01
Ca	mg/l	34.8	8.46	64.0	48.9	0.04
Fe	mg/l	0.03	0.05	2.16	3.63	<0.01
K	mg/l	3.58	0.82	7.72	6.83	<0.01
Mg	mg/l	1.32	0.21	2.98	2.58	<0.01
Na	mg/l	9.27	2.70	15.9	13.3	<0.01
Sb	mg/l	0.002	0.003	0.003	0.004	<0.001
Ag	mg/l	<0.001	<0.001	<0.001	<0.001	<0.001
As	mg/l	0.003	0.001	0.015	0.018	<0.001
Ba	mg/l	0.13	0.22	0.25	0.25	0.09
Be	mg/l	<0.01	<0.01	<0.01	0.01	<0.01
B	mg/l	<0.001	0.001	<0.001	<0.001	<0.001
Cd	mg/l	<0.001	<0.001	<0.001	<0.001	<0.001
Cl	mg/l	46	15	120	100	-
Cr	mg/l	<0.01	<0.01	<0.01	0.97	<0.01
Co	mg/l	0.24	0.11	0.34	1.53	0.11
Cu	mg/l	0.02	<0.01	<0.01	<0.01	<0.01
F	mg/l	5.40	2.2	10	8.9	-
Li	mg/l	<0.01	0.08	<0.01	0.25	<0.01
HPO4	mg/l	<0.20	<0.20	<0.20	<0.20	-
Pb	mg/l	<0.001	<0.001	<0.001	<0.001	<0.001
Mn	mg/l	<0.01	<0.01	0.14	0.06	<0.01
Mo	mg/l	0.48	0.81	0.99	1.14	0.28
Ni	mg/l	3.36	5.41	24.0	38.7	<0.01
Nitrate	mg/l	0.45	0.20	0.74	0.57	-
Se	mg/l	0.006	0.002	0.006	0.006	<0.001
SO4	mg/l	36	13	57	47	-
Sn	mg/l	<0.001	<0.001	<0.001	<0.001	<0.001
Sr	mg/l	0.13	0.05	0.03	0.28	<0.01
Tl	mg/l	0.001	0.002	<0.001	<0.001	<0.001
V	mg/l	0.12	0.12	0.06	0.80	0.08
Zn	mg/l	0.19	0.07	0.05	0.09	0.02

Table 4.2. TCLP Results for Polk Gasification Slag.

Element	Units	Polk Unground	Polk Ground	Blank	TCLP Standard	Drinking Water Standard
Method		TCLP	TCLP	TCLP	-	-
Grams solids		100.1	100.1	0		
Grams liquid		1958.4	1957.8	-		
Liquid/solid		20	20	-		
pH (post filter)		4.96	5.00	4.93		
Element	Units					
Ag	mg/l	0.01	<0.01	0.01	5.0	-
As	mg/l	<0.01	<0.01	<0.01	5.0	0.05
Ba	mg/l	0.02	0.08	0.01	100	-
Cd	mg/l	0.01	0.01	0.01	1.0	0.01
Cr	mg/l	0.07	1.43	0.05	5.0	0.05
Hg	mg/l	<0.0001	<0.0001	<0.0001	0.2	0.002
Pb	mg/l	0.01	0.01	<0.01	5	-
Se	mg/l	0.002	0.006	<0.001	1.0	0.01

Task 5.0 Process Plant Design.

In order to produce 100 tons of carbon form the Eastman slag for testing as recycle fuel, it would be necessary to screen approximately 300 tons of slag. A process plant was designed to complete this objective and a flowsheet summarizing the solids and water balance is shown in Figure 5.1.

The process plant was designed to be fed with a Bobcat loader and conveyor at a rate of 2 to 5 tons per hour into an agitated mix tank. Water is added to produce a slurry containing 17 to 33% solids. The slurry is withdrawn from the base of the mix tank with a centrifugal pump (120 gpm) through a 2" diameter flexible reinforced hose. A portion of the slurry is recycled back into the mix tank to prevent settling while approximately 40 to 48 gpm of slurry is fed onto a 4' diameter Sweco vibrating screen equipped with 3 different size screens. The frit (+28 mesh) is immediately be removed and stockpiled. This product comprises approximately half (by weight) of the plant feed. The fines (-100 mesh) are a dilute slurry (1.4-4% solids) and is discharged into a collection sump. The carbon-enriched fraction (-28+100 mesh) is conveyed into a stockpile where it is allowed to drain. Periodic sampling verifies screening efficiency and the feed rate and solids content of the Sweco feed slurry.

A scaled diagram of the processing plant is shown in Figure 5.2. The Sweco screen was mounted on a 20 ft long trailed that was used to haul equipment to the site. Electrical requirements were met with a diesel generator that was also hauled to the site. Water was supplied from the site water system.
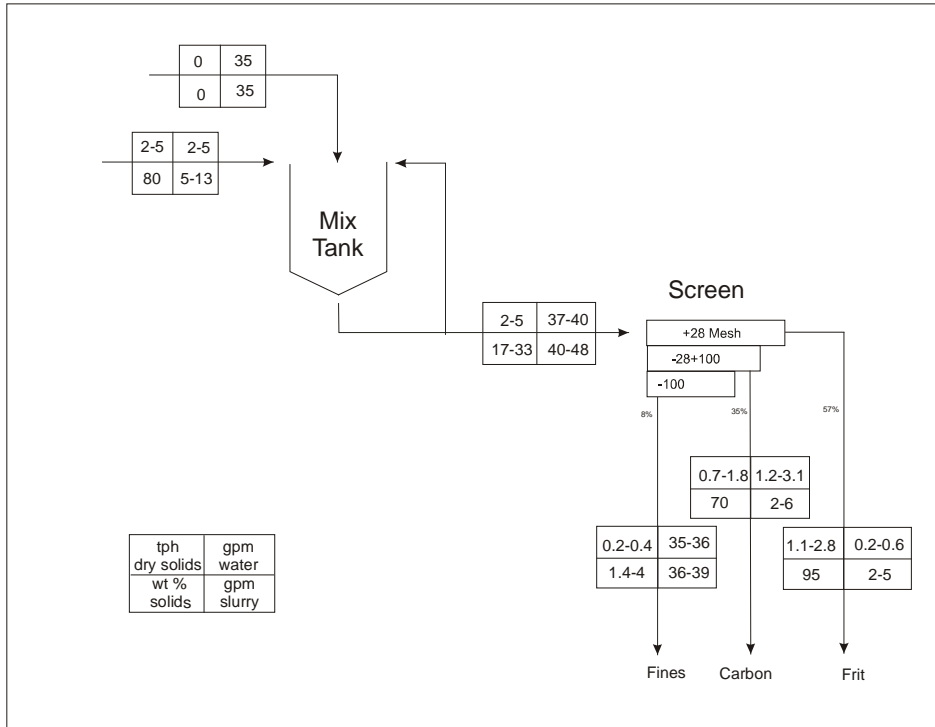
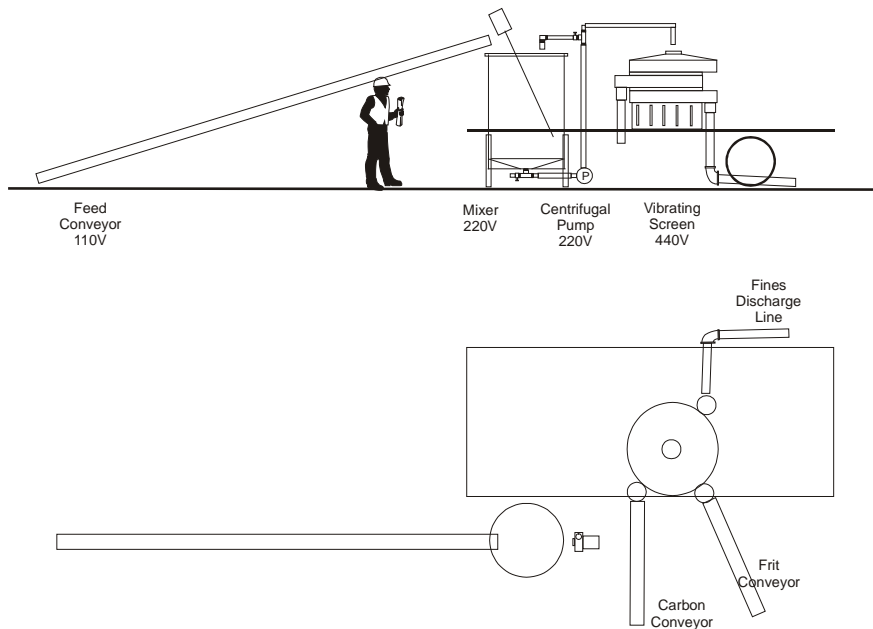Figure 5.1. Solids and Water Balance of Process Plant.

Figure 5.2. Elevation and Top Views of Processing Plant.

Processing plant conceptual design is shown in Figure 5.3 and was based upon the flow requirements and existing operating equipment at the Eastman gasifer in Kingsport, TN. With the current arrangement, slag is periodically removed from the gasifer on a predetermined time cycle through a lock-hopper and dropped into a quench tank. Settled solids (primarily frit and coarse carbon) are removed from the bottom of the quench tank with a drag conveyor that conveys the slag into haul trucks for transport and storage. The quench tank also includes an exit pipe located at approximately half of the quench tank depth. Water and suspended solids, primarily carbon, are removed through the pipe and pumped to a thickener where flocculant is added. Settled solids are dewatered with vacuum drum filters and filter cake is discharged into haul trucks for transport and storage. Thickener overflow water and filtrate are recycled back to the quench tank.

In order to accommodate processing capabilities that are compatible with the existing slag handling facilities, the process flowsheet is fed by the drag conveyor at a design feed rate of 10 tph and fed onto a double deck screen to remove coarse oversize material and produce a coarse frit product. Additional water will be added either into a mix tank and/or directly onto the screen deck as spray water depending upon specific citing considerations. The actual size of the screen openings will depend upon potential end-uses and market specifications, however it is envisioned that the oversize screen will be 4 mesh and the undersize screen will be 80 mesh. Based upon feed characterization, 2.3 tph of frit (-4+80 mesh) will be produced. The screen effluent will report to a sump where it will be pumped into a bank of classifying cyclones to minimize the amount of water reporting to the screen bowl centrifuge which will be fed by the cyclone underflow, producing a dewatered fuel product (5.2 tph at 23% solids). The centrifuge effluent and cyclone overflow report to a thickener where solids settle after flocculant addition and are dewatered into a fine product (2.5 tph at 56% moisture) with a belt filter press. The belt filter press effluent is recycled back to the thickener to recover fine solids and clarified water from the thickener is used as make-up water in the process feed sump.

With this processing configuration, three distinct products are produced, a vitreous frit, a fuel product and a fines product. Carbon is enriched in the fuel product which should contain 58 to 62% carbon. The frit product would be comprised essentially of vitreous slag and contain less than 2% carbon and the fines product would contain 30 to 40% carbon with a high moisture content (56%), however, most of the water is contained in the pore structure of the carbon and does not exist as surface moisture.

One of the primary design considerations for the Eastman site is that each of the gasifiers is already equipped with a drag conveyor to remove slag from the quench tank. Since the conveyors are already in operation, the processing plant was designed to receive dewatered slag from the drag conveyors and removal to accommodate slag processing plant feed is certainly not justified. However, when a new gasifer is constructed and slag processing is considered as a viable operating strategy, installation of the drag conveyors will not be necessary, thus avoiding significant capital and maintenance expenses. For this situation, sump pumps would be used to remove slag from the quench tanks and feed the slag processing plant. A list of proposed equipment for a slag processing plant at Eastman is shown in Table 5.1.

FEED SLURRY

Legend	
tons/hr dry solids	% solids
gal/min water	gal/min slurry

10	26
114	133

MIX TANK
Size To Be Determined

P

10	26
114	133

DOUBLE DECK SCREEN

OVERSIZE

2.3	95
0.4	5

COARSE PRODUCT

7.7	21.5
114	128

CYCLONE

CYCLONE FEED SUMP

P

CENTRIFUGE

5.2	77
6	16

CONVEYOR

FUEL PRODUCT

2.5	8.5
108	112

0	0
84	84

P

THICKENER

P

BELT FILTER PRESS

FINE PRODUCT

2.5	44
13	18

2.5	30
23	28

0	0
10	10
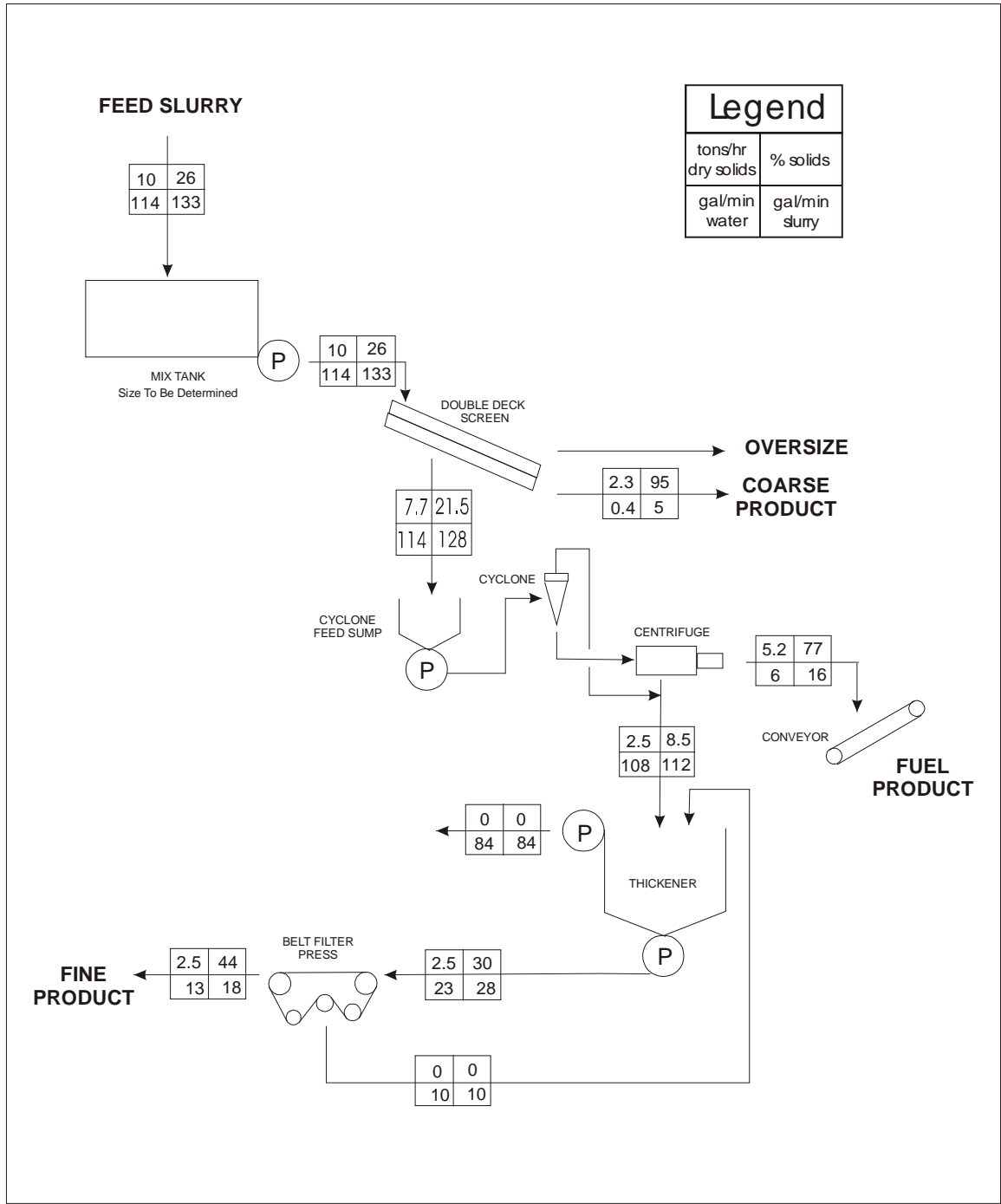
Figure 5.3. Conceptual Design of Processing Plant for Eastman Gasifier Slag.

Item Number	Item	Comment
1	**Feed Hopper**	**Charged with rubber tire front end loader**
2	**Belt Conveyor**	**From feed hopper to agitation tank**
3	**Agitation tank**	
4	**GIW Pump**	**From agitation tank to screen**
5	**1 Lot piping**	
6	**Double Deck Primary screen**	**Innovative**
7	**Concrete retaining blocks**	**For storing coarse aggregate from primary screen**
8	**Primary screen collection sump**	
9	**GIW pump**	**From primary screen sump to cyclone**
10	**1 Lot piping**	
11	cyclone	**Krebs**
12	**Centrifugal dryer**	
13	**Belt conveyor**	**from dryer discharge to fuel storage area**
14	**Concrete Retaining Blocks**	**for storing fuel produced on centrifuge**
15	**2 Lots Piping**	**combined cyclone overflow with dryer underflow to thickener**
16	**Thickener**	
17	**GIW pump**	**grey water from thickener back to plant**
18	**1 lot piping**	**grey water from thickener return to plant**
19	**GIW Pump**	**thickener underflow to belt press**
20	**1 Lot Piping**	**thickener underflow to belt press**
21	**Belt press**	
22	**Belt Conveyor**	**filter press to fines storage area**
23	**Concrete Retaining Blocks**	**for storing fines produced by filter press**
24	**Chemical Feed System**	**for fines settlement in thickener tank**
25	**Structural steel**	
26	**Electrical controls system**	
27	**Electrical control systems building**	
28	**Nuclear density flow meter**	
29	**Plant Electrical & Plumbing Infrastructure**	
30	**Misc. Concrete Slabs and Foundations**	
31	**Enclosure Building for Entire Processing Facility**	
32	**Lab/Testing Equipment**	

Table 5.1. Equipment List for Eastman Gasifier Slag Processing Plant.

Task 6.0 Proof of Concept (POC) Field Processing Plant.

In order to evaluate the feasibility of utilizing processed gasification slag as recycle fuel in the Eastman Chemical gasifiers, it was necessary to generate sufficient frit and carbon products from the mixed slag. Eastman technical personnel decided that recycle testing in the commercial gasifiers will initially be conducted with recovered frit, rather than recovered carbon. The primary reason for this decision is the concern that since the recovered carbon product has a higher ash content than the typical feed coal (35% ash v. 7% ash), the introduction of the higher ash content carbon may diminish CO yield. Since CO is the essential component of the syngas produced by the gasifier, rather than risk reduced CO production, the safer alternative would be to introduce frit at a rate to mass balance the ash in the gasifier feed.

The site selected for slag processing activities was the contaminated soil storage area on the North Long Island. Since this site is located within the production area of the Eastman Chemical facilities, it was necessary for CAER personnel to complete a required 4 hour Contractor Safety Training class to facilitate access to the site. Upon completion of the Contractor Safety Training class, trailers and equipment were delivered to the site and assembled. An initial load of gasification slag (20 tons) was delivered and processing commenced. A diagram of the site layout is shown in Figure 6.1.

The slag was fed into the feed hopper and conveyed into a 500 gallon mix tank and slurried to 10% solids using a mechanical stirrer. The slurry was withdrawn from the base of the feed tank with a centrifugal pump through a 2" line (100 gpm) and recycled back into the tank to maintain mixing. A portion of the recycled slurry (20 gpm) was diverted onto the Sweco screen which was equipped with 28 mesh and 100 mesh screens. The +28 mesh material (essentially frit) was recovered and transferred to a stockpile, the -28+100 mesh solids (essentially carbon) was recovered on a conveyor belt and stockpiled while the -100 mesh slurry (essentially high ash carbon) was discharged to the floor drain and processed through the site waste water treatment plant.

Some operational problems were encountered during the initial processing, most notable the inability of the sticky carbon product (-28+100 mesh) to be discharged from the belt, causing significant draining from the return belt. This problem was remedied by eliminating the conveyor and collecting the carbon product in wheel barrows. Another problem was encountered when the primary mixer overheated, causing the coarse frit to settle in the slurry mix tank and plug the discharge port. This was remedied by using a smaller diameter agitator on the mixer. Approximately 10 tons of slag was processed during the initial start-up and resulted in the production of approximately 4 tons of frit and 5 tons of carbon which were stored in separate stockpiles
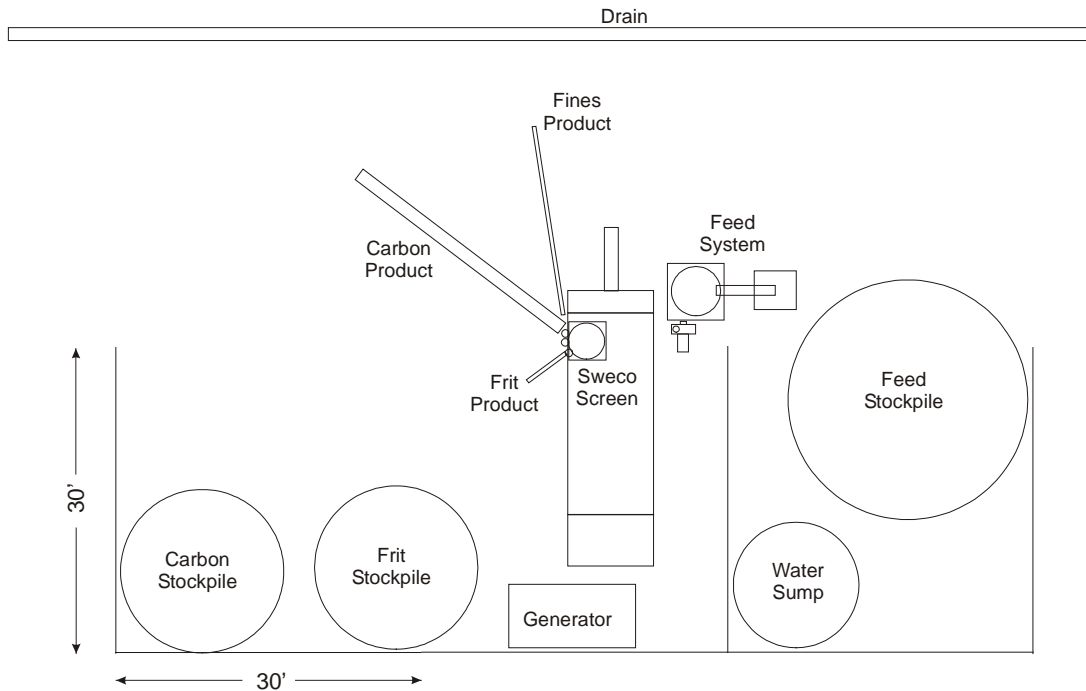
Figure 6.1. Processing Plant Site Layout.

In order to eliminate the constant problems associated with feed pump plugging and increase the throughput of the processing plant, it was decided to remove the slurry tank and convey the feed slag directly onto the Sweco screen. An array of spray nozzles were arranged over the top screen to facilitate screening to remove fine solids. This approach proved to be much more effective and was used throughout the remaining screening activities.

Random samples of the frit and carbon screen products were taken every 30 minutes and separately combined into composite samples, which were analyzed to determine screen performance. A summary of the results for the frit product is shown in Figure 6.2. When the slurry feed system was used initially, the frit product contained 88% +28 mesh and 1.4% -100 mesh. When the slag was fed directly onto the screen, results were not as good (82% +28 mesh and 3% -100 mesh). Water spray nozzle type and arrangements were changed to improve screening results in order to minimize the amount of fines remaining in the frit screen product, and by mid-January, results were actually better than what was obtained with the slurry system (94.5% +20 mesh and 0.8% -100 mesh).

Figure 6.3 summarizes sample evaluation of the carbon products. The objective was to remove as much of the -100 mesh material as possible since this size fraction had a higher ash content. Results were similar, with 8 to 10 % -100 mesh in the carbon product, despite the spray arrangement.
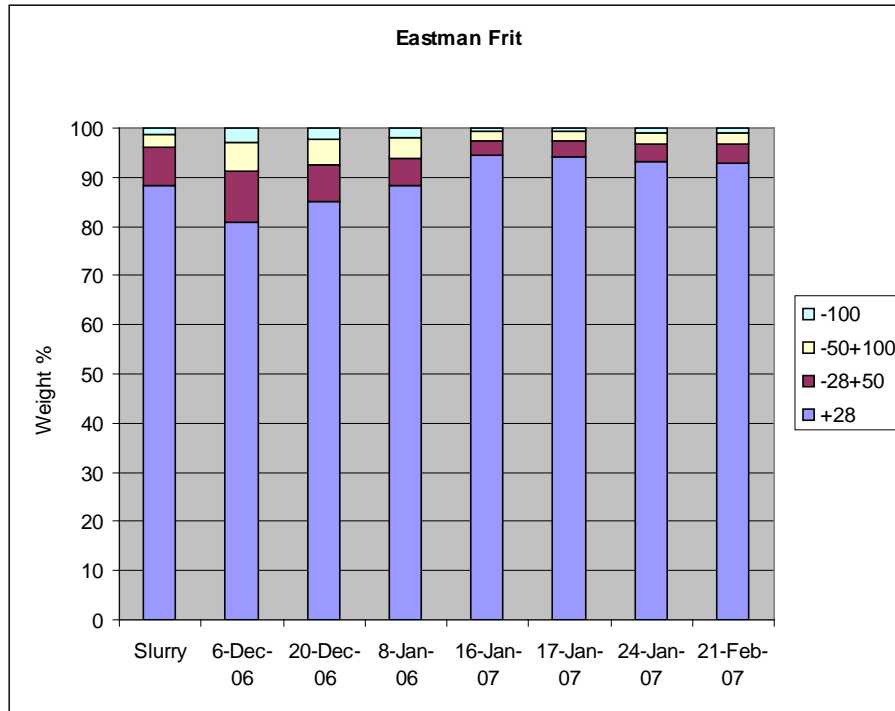
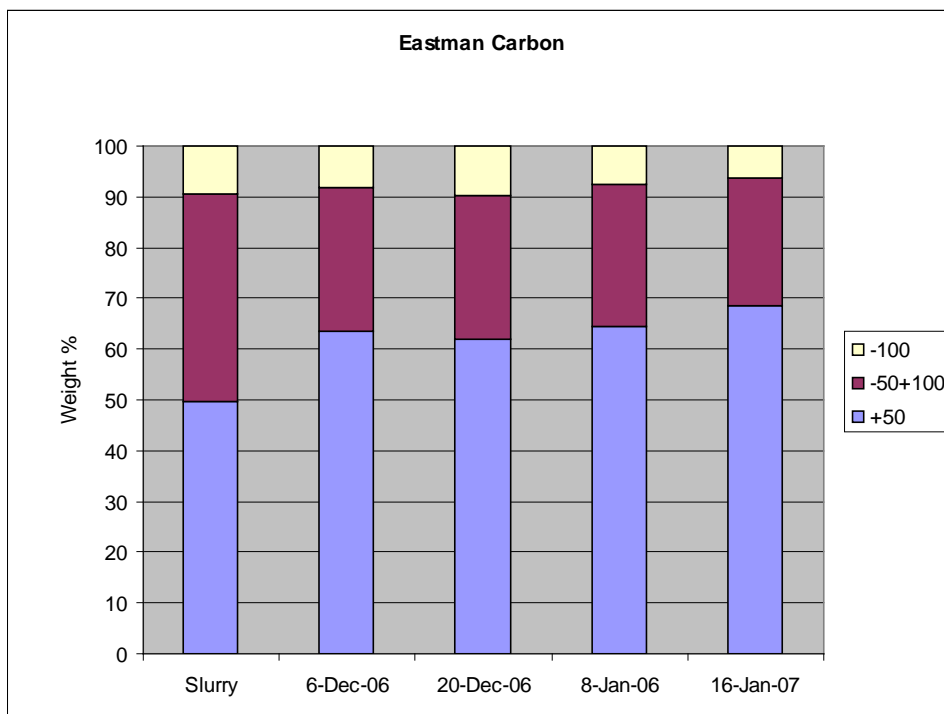Figure 6.2. Size Distribution of Eastman Frit Products.

Figure 6.3. Size Distribution of Eastman Carbon Products.

The grade of the frit and carbon screen products is summarized in Figure 6.4. When the slurry feed system was used initially, the frit product contained 7.2% LOI while the carbon product contained 58.6% LOI. After the water spray arrangement was optimized, the frit product consistently contained less than 5% LOI while the carbon product was also consistent with 62 to 63% LOI.
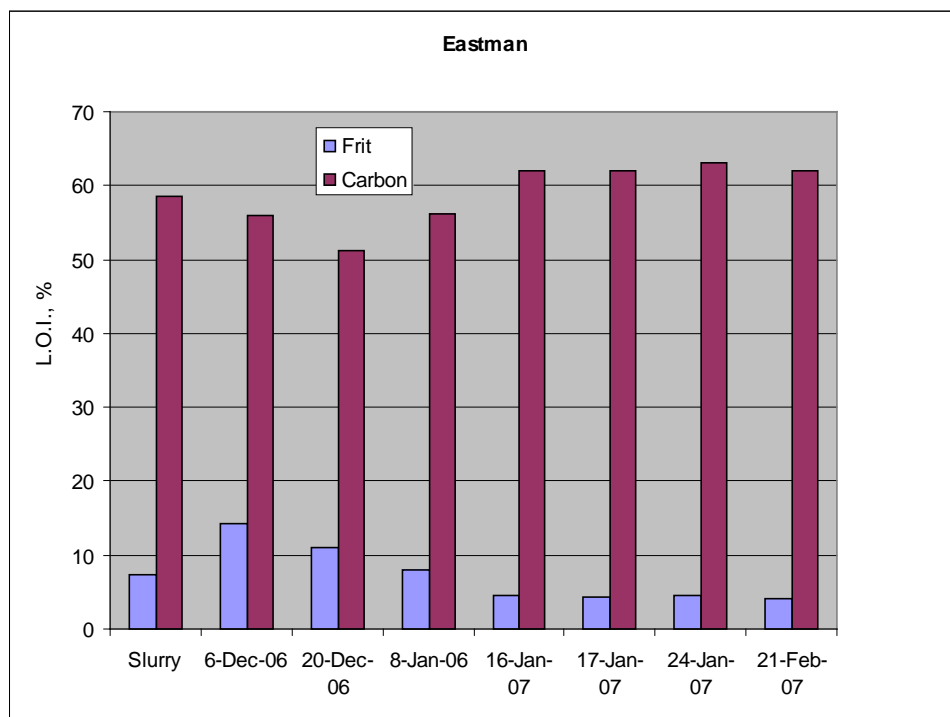

Figure 6.4. Grade of Eastman Frit and Carbon Products.

A summary of screen throughput is shown in Figure 6.5. As previously described, when the 20 ton slag loads were delivered to the test site, they were allowed to drain. Portions of the pile were saturated while other portions were much drier. A series of tests were conducted by feeding consistent moisture sections of each load to determine screen throughput. Samples were taken to determine the feed moisture, and the feed rate was changed to achieve the desired result of less than 5% LOI in the frit product and greater than 60% LOI in the carbon product. Results show that as the feed moisture was increased from 40% to 54% moisture, the throughput increased from 1.3 to 3.2 tons/hr while maintaining consistent product grades. Screen capacity at 40% feed moisture was 123 lb dry solids/hr/ft^2 , which increased to 326 lb dry solids/hr/ft^2 as the feed moisture increased to 54% solids. These results clearly show the increased throughput of wet screening as well as the benefit that could have been realized if the screen was fed as a slurry. This was not possible due to equipment limitations, but will certainly be recommended for commercial-scale processing.
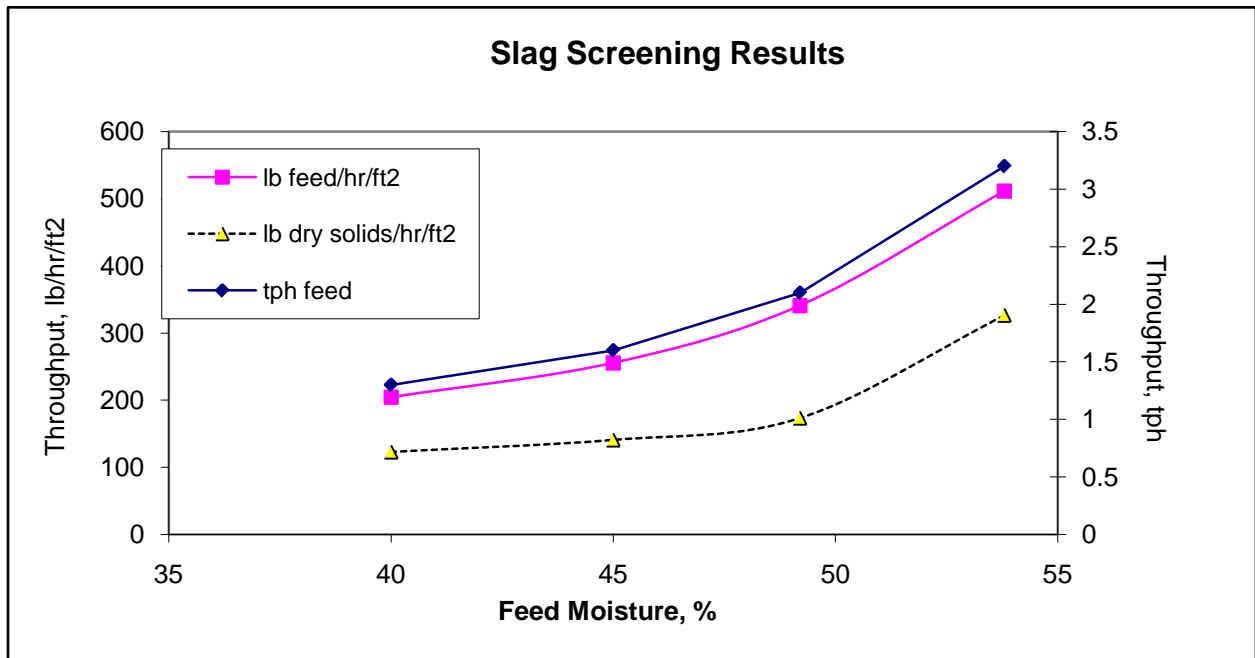
Slag Screening Results

Figure 6.5. Summary of Slag Screening Throughput.

Task 7.0 Large Volume Testing of the Char Material as Gasification Recycle Fuel.

Reuse of Char in Gasification

Carbon conversion in a gasifier reactor chamber is a function of many parameters including: grind size, amount of moderator, reactor geometry, feed injector mixing, feed chemistry, and oxygen to feed ratio (O:C).   In a slurry-fed gasifier, the amount of solids in the slurry will also impact conversion and syngas composition.   Depending on the final use of the syngas, all of these parameters need to be balanced to maximize economics of a given plant. For instance, a chemical plant can debottleneck if the amount of CO_2 can be reduced while increasing the CO content of the syngas. For an IGCC unit that can utilize CO_2 for power production to provide mass and cooling to the combustion turbine, additional CO at the expense of CO_2 may be less important.

Much of the gasification process involves collecting and removing solid material from the water and gas streams. The solids produced during gasification include slag, flyash, char, and soot. These materials are often mixed together, leading to disposal and economic issues for a given plant. While these materials have been readily separated over the past 28 years at different plants, separation schemes that lead to double or triple handling, poor separation, impacts on plant environmental compliances, or reduction in reliability are not going to be pursued.   The most cost effective design would be to integrate the separation scheme within the gasification process.

Plant Economics

Gasification models indicate that by decreasing the amount of moisture entering the gasifier, more CO and less CO_2 is generated in the syngas under equilibrium conditions. Commercial plant operations have confirmed these models. Also, with a slurry-fed gasifier, as water is removed from the slurry, the gasifier temperature will increase at a given O:C ratio. If the ash/slag composition can't be controlled, the increase temperature can lead to higher refractory wear in a hot wall (refractory lined) reactor, or stickier ash particles in a cold wall design which may foul downstream equipment. Ultimately, the O:C ratio may need to be reduced, or additional cooling fluids brought into the process to decrease the syngas temperature. Depending on other conditions, a decrease in O:C can yield more beneficial $(CO+H_2)$ syngas. However, the additional syngas may be produced at the expense of lower carbon conversion in the process. As long as the revenue from the additional good syngas covers the cost of the unconverted carbon, plant economics would dictate to run at a lower conversion. Table 7.1 llustrates several hypothetical cases based on operating trends and computer models.

Table 7.1 Simplified Cost Differential.								
Case	Temp ^{o}F	Refractory Savings	Good Syngas	Carbon Conversion	Feed/Disposal Savings	CO_2	Erosion/ Fouling	Total Delta
High Conversion	2550	0	0	97%	$560K	+2%	$200K	$760K
Low Conversion	2500	$400K	2,000K	92%	($840K)	-1%	($500k)	$1,040K
High Solids	2550	0	4,000K	90%	($1,400)	-2%	($700K)	$1,900K
Low Solids	2500	$400K	0	95%	0	+1%	0	$400K

Assumption: 1000 TPD of feed, 350 days @ $50/ton coal and $30/ton disposal cost.

The biggest unknown cost factor is plant design. For instance, a single gasifier with hotwall refractory will need to replace refractory which may require a 24 day outage. The loss of roduction may warrant a lower operating temperature to decrease the economic impact of the outage by staging it during a mandatory turbine inspection. A multi-train plant may have less concerns about timing, but have issues with solid handling costs. If the plant equipment was designed for 99% single pass conversion, and conversion was lower than this, then the plant may be forced to take unscheduled shutdowns, or operate hotter to prevent fouling of the water system. Extended or numerous shutdowns will quickly eliminate other savings.

Char

The term char refers to partially converted pieces of coal/petcoke particles that have passed through a gasifier reactor partially reacted. Soot refers to particles formed during gas phase interactions. Upon entering the reactor, the volatiles within a particle will vaporize leaving the particle enriched in carbon while lowering its hydrogen, nitrogen, and oxygen content. The particle will also undergo changes to its surface chemistry and porosity as the intense heat alters the particle's structure. At this point, if the particle is ejected from the reaction zone, further reaction will cease.

Another characteristic that will impact the separation and use of the char will be size distribution. If the char is fine, it will impact slurry transport differently than coarser particles. Also, if the char particle developed greater porosity, the particle can hold more water than the

original feed particle. The net result is that the char is different from a similar size coal particle, thus, laboratory testing is required to determine the impact on reusing it within or outside of a gasification plant.

Char/Ash Distribution

As a coal particle reacts, the ash within it will melt to form a molten or semi-molten droplet depending on the original mineral constituents. If the ash particle hits the wall, a molten slag layer will form. Otherwise, the ash sphere leaves with the gas to form a flyash particle. The char, flyash, and slag shards will mix together in a downward, entrained gasifier. During single pass operation, the composition of the collective solid will depend on the carbon conversion and ash amount in the feed. At high carbon conversion, the solids will have a high ash concentration, making reuse uneconomical. If more of the coal ash becomes flyash versus coarse slag, and the char size is small, then separation techniques may need to be changed to properly collect and segregate the materials.

If the char is recycled back to the gasifier, and the ash content is high, additional slurry must be pumped to the unit to maintain the carbon balance. Pumping more slurry causes two negatives: i) more water enters the gasifier causing more CO_2, and ii) ash will act as a moderator and cool off the gasifier. If the ash melting point is close to operating temperature, additional heat must be supplied to melt the ash which equates to more CO_2. Therefore, instead of recycling all material back to the gasifier, separation of the fine ash and char may be more advantageous.

Coal Slurry

As previous indicated, the final composition of the syngas is impacted by the solid loading in the slurry. The collective properties of the solid particles will impact slurry stability and viscosity. Slurries that settle out quickly can lead to line pluggage. Viscous slurries could create pumping and atomization issues. In the worse case, a viscous, unstable slurry can form. If any of the material sent to the grinding mill contains salts or other chemicals, both stability and viscosity can be adversely impacted as well as increasing corrosion rates in the mill circuit. Chemicals can be added to the slurry to improve both viscosity and stability, but these chemicals cost money and work in a narrow range.

Most slurry work has indicated a bi-modal particle size distribution leads to the best slurry conditions. The packing of smaller particles between larger particles will tend to keep the large particles in suspension, while the large particles tend to keep the smaller particles from coagulating. Reaction kinetics would dictate that the particles should be ground as small as possible to reduce residence time in the reactor. However, smaller total distribution increases viscosity which impacts injector droplet size as well as pumpability. Once the optimal grinding point is found, any changes in feed will require readjustment to reduce the impact on operations. The worse case for gasifier operations would be to return a high ash, fine particle size, porous, chemically altered material back to the gasifier if the plant is interested in CO production and long term reliability. At the same time, with increased feed stock and land filling costs, a large negative impact on operating costs will occur.

Eastman Gasification

Eastman's syngas is used for the production of acetyl chemicals (methanol is also generated and consumed in the acetyl stream). As such, higher CO in the syngas will yield more

chemicals for a given quantity of oxygen and coal. Eastman also operates far above reactor design rates to maximize production. Higher CO_2 or H_2 to CO ratios can be limiting by impacting acid gas removal, pressure drops in lines, compressor efficiency, etc. The net result of Eastman's process improvement efforts is that CO_2 in the syngas has been minimized to achieve record chemical production without increasing plant size. Eastman's goals of working with the University of Kentucky were to: i) attempt to reduce coal cost while maintaining high gasifier rates by recycling the char, and ii) increase landfill capacity by finding a buyer for the slag. These two goals required characterization and testing of the various fractions of the solids. Decreasing coal and disposal cost at the expense of chemical production is not an option at current economics.

Unlike earlier work on char and ash separation conducted at Tampa Electric, Eastman had little desire to use the gasification char as boiler feed. The high sulfur and iron content in the ash and char will cause issues within nearby PC boilers. Double handling of the char by multiple stages of separation and drying also creates environmental and operating issues around a gasification plant. Consequently, the best choice for Eastman's gasification char is either to feed it back to the gasifier, or use it as fuel in a cement plant. Based on previous discussions with cement plants, limited interest was expressed mainly based on transportation cost and moisture.

Slag Separation

As a preliminary step, CAER's data on distribution of Eastman's solids were reviewed to determine possible impact on operations. Eastman's performance models indicated that as long as the carbon content remained similar to the original feedstock, more CO could be generated in that the overall H_2 content of the feed stream was reduced by displacing coal with char that already had lost H_2 during gasification. The slight cooling of the reaction temperature predicted by the model due to a higher ash content also favored less CO_2 generation.

Past experience on recycling material back to gasifiers has been collected for over 25 years from commercial plants. In most cases, slurry production and gas compositions were impacted because of the increased ash content, reduced particle size, and changed chemistry as mentioned previously. Additional work needed to be conducted to better define possible economic losses. Therefore, prior to doing a major demonstration run at the plant, slurry testing and demonstration of the char separation technique had to be proven. The University of Kentucky brought a skid mounted separation unit to Eastman's site to obtain possible material for a demonstration run.

Based on preliminary analyses of TECo's and Eastman analyses, much of the carbon content by weight resided in the -20 to +100 mesh split. Recycling all the material back to the gasifier similar to TECo's operation would greatly impact CO production. An initial concern was that the -20/+100 split still had a significant portion of ash in it that reduced the carbon content below that of the coal. If the carbon content could not be increased, then recycling this stream at Eastman would result in a negative economic penalty at a period of high chemical demand.

The solid's ash content consisted of fly ash, glass shards, and residual ash contained in the char particles. UK was contacted concerning removal of the ash, but because of the narrow size fraction split and morphology of the particles, simple gravity separation was going to be difficult. Froth flotation may improve the concentration, but this would increase separation cost. In Eastman's case, the solids can be sent to a pre-existing landfill, thus, any capital cost must compete with this existing option. In addition, without any known buyers for the coarse slag in

the area, revenue streams could not be counted on to support separation of the coarse slag only.

Once the carbon-rich split was obtained from the skid unit, Eastman also began conducting slurry testing by preparing several coal slurries at different recycle amounts (Fig 1). The slurry work indicated that by returning a high fraction of fines to the coal slurry, the viscosity would increase significantly. Several chemical additives were tried to improve the viscosity, but none appeared to work. The slurries were prepared by both adding material before and after grinding. No apparent differences were noted.
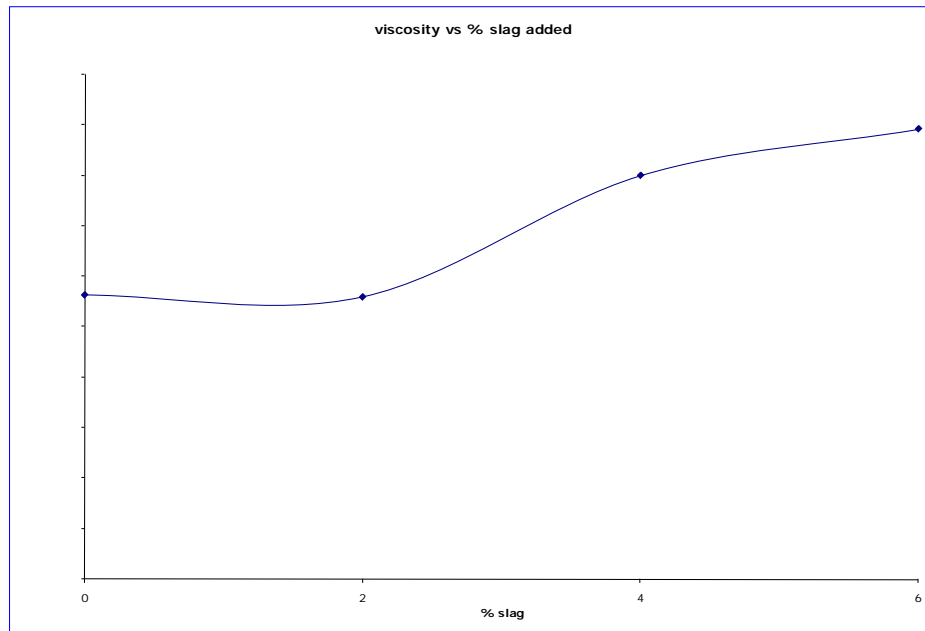

Figure 7.1. Viscosity change versus fines addition to commercial slurry**.**

The impact on the slurry concentration was not unexpected based on previous work. The bimodal slurry distribution was altered towards the fines. In addition, the char's porosity allowed the char to contain more water, or adsorb water out of the slurry (if introduced dry). In either case, the slurry concentration will decrease for a given viscosity and water content.

Conclusion

Eastman's intent for this project was to assist the University of Kentucky and Department of Energy to improve the economics of gasification by reducing landfill and feedstock cost, but not at the expense of Eastman's commercial operations. If a suitable carbon-rich split could have been generated, a trial run would have been conducted to obtain commercial data. However, after analyzing laboratory results and comparing to proprietary operating data, the impact on carbon monoxide production would have resulted in a steep economic penalty. Additional separation of the solids is needed if the ash content of the feed is high. In addition, the lack of marketing opportunity for the slag yields a negative NPV based on the capital for the equipment. For new plants in design, the economics will be different allowing for different solid handling opportunities.

Task 8.0 Large Volume Uses of Vitreous Frit in Cement Manufacture.

Testing was initiated to determine the feasibility of using vitreous frit recovered from the Eastman slag as raw feed for cement clinker manufacturing. The equipment necessary to conduct these experiments was acquired and a series of preliminary experiments were conducted in order to establish a reproducible procedure that would provide meaningful results. A Lindberg GS tube furnace was used with the temperature program set at 20°C/min in order to reach the desired temperature of 1400°C and hold the temperature for two hours.
The established procedure was a follows.

The total raw sample mass that could be placed in furnace crucibles was determined to be 60 grams. Various proportions by weight percent of raw materials were mixed by hand using a pestle and mortal for 20 minutes and approximately 20 grams of homogeneous ground sample was spread into three crucibles. The mix proportions were comprised of Eastman slag, hydrated lime and Ottowa sand in combination to provide the desired chemical composition for the clinker that would be produced. The composition of the raw ingredients are summarized in Table 8.1, while the composition if the expected clinker is shown in Table 8.2. Each crucible was placed in the outer end of the furnace tube for 20 minutes to prevent the crucible and furnace tubing from cracking dure to thermal shock. The front and rear crucible temperature was 900°C and 700°C respectively.   After 20 minutes, the sample boat was pushed into the center portion of the furnace where the temperature was 1400°C for 10, 20, and 30 minutes respectively, for each crucible. After the desired time at 1400°C the crucibles were removed from the furnace and allowed to cool to room temperature. Once the crucibles cooled, the formed clinker was removed and grounded to a fine powder using using a ring mill. The powdered samples were then analyzed to determine insoluble residue, free lime and crystal structure by XRD using Phhilips X-Ray Diffraction Spectroscopy (XPert) loaded at 45KV and 40 mA.

The free lime for the first set of tests (10, 20 and 30 minutes at 1400oC) ranged from 6.64% to 9.84% and the Insoluble Residue from 3.74% to 7.83% as shown in Table 8.3. The very high Insoluble Residue may be attributed to contamination from the sample boat since the clinker is partially melted and fused into the ample boat surface. When the clinker was scraped out of the cooled crucible, it may have also contained some refractory materials. This can be confirmed from second set of tests (20 minutes at 1400°C) where the clinker was carefully removed form the crucibles without scraping. In these tests, the free lime contents for all three clinkers match the first run, but insoluble residue was much lower that the first run (0.45% to <0,05% Insoluble Residue).
One basic conclusion that can be drawn from these results is that the longer the residence time in the tube furnace, the lower the concentration of free lime in the clinker. XRD analyses of the clinker samples also confirmed the presence of Ca3SiO5, Ca2SiO4 Brownmillerite, and CaO, however the primary composition was comprised of the desirable components Ca3SiO5 and Ca2SiO4.

Table 8.1. Raw Materials Used to Produce Clinker.											
	Wt. %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	P_2O_5 %	TiO_2 %	SO_3 %	LOI %
Hydrated Lime	77.5	3.83	1.56	0.45	68.44	2.06	0.12	0.09	0.02	0.1	0.15	23.27
Eastman Slag	11.5	38.13	20.32	26.70	1.94	1.14	0.32	2.30	0.10	1.00	1.43	5.00
Ottowa Sand	11.0	99.70	0.06	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	0.10	<0.01	0.10

Table 8.2. Expected Clinker Composition.										
Expected Clinker	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	P_2O_5 %	TiO_2 %	SO_3 %
	22.25	4.37	4.21	65.55	2.13	0.16	0.41	0.04	0.24	0.34

Table 8.3. Free Lime, Insoluble Residue and XRD Scan of Clinker Products.			
Sample ID	Free CaO %	Insoluble Residue %	XRD Scan
10 mins clinker 9-26-07	9.84	3.76	Ca_3SiO_5,Ca_2SiO_4, CaO, Brownmillerite, MgO
20 mins clinker 9-26-07	6.57	3.74	Ca_3SiO_5,Ca_2SiO_4, Brownmillerite, CaO,MgO
30 mins clinker 9-26-07	6.64	7.83	Ca_3SiO_5,Ca_2SiO_4, Brownmillerite, CaO,MgO
10 mins clinker 10-23-07	8.54	<0.05	Ca_3SiO_5,Ca_2SiO_4, CaO, Brownmillerite, MgO(trace)
20 mins clinker 10-23-07	5.30	<0.05	Ca_3SiO_5,Ca_2SiO_4, CaO, Brownmillerite, MgO(trace)
30 mins clinker 10-23-07	6.15	0.45	Ca_3SiO_5, CaO, Brownmillerite, Ca_2SiO_4, MgO(trace)

Conclusion

Samples of coal gasification by-products produced at Polk Station and Eastman Chemical were obtained and characterized. It was found that slag components form both sources distinctly partitioned by size. Vitreous frit was concentrated in the coarse +20 mesh fraction while high carbon char predominated in the -20+100 mesh fraction.

The vitreous frit component showed several potential for utilization in several areas, namely as concrete aggregate, cement clinker feed and as a pozzolan. When evaluated as concrete aggregate, neither source showed significant potential for undergoing alkali-silica reactions which could produce harmful internal expansion in concrete. When tested as a component of cement kiln feed, the clinker produced was comprised primarily of the desirable components Ca_3SiO_5 and Ca_2SiO_4. Before the vitreous frit can be considered for use as a pozzolan, fine grinding would be necessary. Energy consumption is estimated to be a minimum of 60 kwhr/ton. Grinding studies showed that the energy requirement for grinding the Polk slag

were slightly higher than for the Eastman slag. Both of the fine-ground slag samples showed pozzoalnic activity in mortar cube testing and met the ASTM C618 strength requirements after only 3 days. Pozzolanic activity was further examined using British Standard 196-5 and results suggest that the Polk slag was more reactive than the Eastman slag.

A processing plant was designed to produce 100 tons of carbon from the Eastman slag to conduct evaluations for use as recycle fuel. The processing plant was mounted on a trailer and hauled to the site for use. Two product stockpiles were generated; the frit stockpile contained 5% LOI while the carbon stockpile contained 62% LOI. The products were used to conduct recycle fuel tests.

A full-scale processing plant was designed to separate the slag produced at Eastman into 3 usable products. The coarse frit has been shown to be suitable for use as clinker feed for producing Portland cement. The intermediate-size product would be enriched in carbon (58-62% C) and may be used as recycle fuel either in the gasifier or in a PC boiler. The fines product contains 30-40% C and may also be used as a recycle gasifier fuel, as is presently done at TECO's Polk Station, however, due to gasifier operating requirements, this may not be feasible at Eastman.

Eastman's intent for this project was to assist the University of Kentucky and Department of Energy to improve the economics of gasification by reducing landfill and feedstock cost, but not at the expense of Eastman's commercial operations. If a suitable carbon-rich split could have been generated, a trial run would have been conducted to obtain commercial data. However, after analyzing laboratory results and comparing to proprietary operating data, the impact on carbon monoxide production would have resulted in a steep economic penalty. Additional separation of the solids is needed if the ash content of the feed is high.

List of Abbreviations

ASTM	American Society for Testing and Materials
C	Carbon
CAER	Center for Applied Energy Research
d_{50}	Average Particle Size
DTMS	Davis Tube Magnetic Sparator
ICP-MS	Inductively Coupled Plasma-Mass Spectrometer
kW	Kilowatts
LOI	Loss-on Ignition
PC	Pulverized coal
RCP	Rapid Chloride Permeability
RPM	Revolutions per Minute
TECO	Tampa Electric Company
UCS	Unconfined Compressive Strength
UK	University of Kentucky
XRD	X Ray Diffraction