

Final Progress Report

Project Title: R&D of Novel Materials for Animal Litters Using High Carbon Fly Ash Final Progress Report

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Task A: Synthetic Zeolite Formation Baseline Studies

1. Actual Accomplishments:

Task A-1.1: Fly Ash Procurement: Several samples of fly ash were obtained from various coal-fired power plants in the US. Both Class C and Class F type fly ashes were procured, as well as several samples of non-concrete spec fly ash including spray-dryer ash. This task was completed in Q3 FY10.

Task A-1.2: Fly Ash Characterization: Each of the procured samples of fly ash procured in Task A-1.1 was analyzed for the major and minor oxides, carbon content, and heavy metals content. Several of the procured samples were submitted for particle size analysis, X-ray diffraction, surface area (BET method), and SEM analysis. Thorough characterization of the fly ash samples was critical for determining which chemical composition was used in each of the experiments. This task was completed in Q3 FY10.

Task A-1.3 & A-1.4: Ion Exchange Synthesis of Parent Fly Ash & Characterization: The ion exchange capacity of the parent fly ash samples was determined. The procedure for testing the cation exchange capacity (CEC) of fly ash (A-1.3), zeolites (A-2.3), or hierarchical zeolites (A-3.3) was the same. Therefore, we have combined the procedure and results of the testing of these 3 classes of materials into a single section. Task A-1.3 and A-1.4 are complete.

Task A-2: Advanced Support (Zeolite) Development:

Task A-2.1: Fly Ash to Zeolite Synthesis: Throughout this fiscal year we began to synthesize zeolites from coal fly ash. The ultimate goal of this task was to design a process that could produce one (or several) commonly used zeolites in a reproducible manner, regardless of the parent fly ash used in the synthesis process. There are in excess of 200 synthetic zeolites known; however, we knew from literature reports that using fly ash as a starting material would yield only a few of these zeolites. Based on the literature reports, the processing conditions for synthesis were widely varying, and therefore resulting in various zeolites made. Our goal was to make high surface area materials by expanding upon the knowledge of the literature. We have successfully designed, and repeated on multiple occasions, the ability to make zeolites from coal fly ash. Our process has shown to be reproducible (in terms of surface area, pore size, etc.) using three as-received fly ash samples; Delta, EWB, and MRT-F. During this fiscal year, we have successfully developed a process for reproducibly creating high-surface area

zeolites using fly ash waste materials as the starting material. Our specific process for making our particular high surface area zeolites from fly ash will not be patented, but rather will be treated as a trade secret within Ceramatec. As we apply these materials to specific applications the process for making the zeolites will become more refined. Task A-2.1 was completed in FY 10.

Task A-2.2: Characterization of Zeolite Fly ash (ZFA) Materials Synthesized: Throughout Task A-2.1, numerous samples were synthesized from multiple sources of fly ash. Each sample created was characterized and classified in this Task. Our typical characterization methods include surface area, pore diameter, pore volume, particle size, XRD (to determine the primary zeolite phase), and CEC. Numerous samples were synthesized during this program; however, the three most common zeolites fabricated in our lab are Ceramalite C11, C21 and C71, which are all high surface area materials. Table 1 below shows the material properties for two of these zeolite structures. We will continue to characterize each subsequent batch made in our labs, and we will add the data to a main database, such that we can continue to build upon the volume of data collected to enable further statistical analysis. This task was completed in FY 10.

Table 1. Characterization of Zeolites made from fly ash.

	C21	C71
Parent Fly ash	MRT-F (S_A - 2.74 m^2/g)	EWB (S_A - 3.37 m^2/g)
BET Surface area(m^2/g)	400	452
Pore Diameter (nm)	3.39	3.77
Pore volume(cm^3/g)	0.12	0.16
Major Phases /zeolites	Faujasite (FAU)	Faujasite (FAU)

Task A-2.3: Ion Exchange Synthesis of Zeolites & A-2.4 Characterization:

Several conventional zeolites synthesized from fly ash during Task A-2.1 (and several hierarchical zeolites synthesized in our laboratory Task A-3.1) were subjected to ion exchange synthesis for two different prospective applications:

1. Cation exchange for modifying zeolite properties
2. Heavy metal ion exchange for waste water purification

Application 1: Cation exchange (Two way exchange): The Na^+ cation native to the zeolite structure is exchanged using another monovalent (i.e. K^+) or divalent cation (Ca^{2+}). The procedure for the cation exchange is shown in Table 2. The resulting ion exchanged zeolite is analyzed for the amount of the foreign cation, as determined by the corresponding cation exchange capacity (CEC) of the material. The CEC values are reported in Table 3. The initial set of experiments included ion exchange using a potassium chloride (KCl) solution. Furthermore, to establish baseline values of

ion-exchange capacity the experimental procedure was repeated for the as-received or parent fly ash samples (Task A-1.3), and we also tested commercial zeolite 13X.

Table 2. Procedure for Ion exchange synthesis using KCl

Step 1: A 0.1 M solution of KCl is prepared by dissolving a known amount of KCl in DI water

Step 2: To 1 g of Ceramalite (zeolite /hierarchical zeolite) 100 cc of 0.1 M KCl solution is added and the contents are transferred to a conical flask.

Step 3: The contents are left under stirring for 24 hr at room temperature and the ion exchanged zeolites synthesized at Ceramatec (ceramalite) is recovered by vacuum filtration and dried in oven for 24 hr at 100°C for further analysis.

The CEC values obtained for potassium exchanged zeolites were found to be higher than their counterparts, which indicates that potassium has the greatest ion-exchange with Na in the zeolite structures. The exchange rate was the highest for commercial 13X, followed by Ceramalite C11 and C71. As expected, the as-received fly ash samples (MRTF, EWB and Delta), which do not contain any crystalline pore structure or any replaceable Na ions, showed very low K ion exchange capacity as indicated by their small CEC values. It can be concluded that in general, the CEC values for potassium exchanged zeolites (those treated according to the procedure outlined in Table 2) exceeded the measured values for the samples that were not ion-exchanged (i.e. pre-ion exchange with K⁺). This testing was completed in FY 11.

Table 3. CEC values of K⁺ exchanged Ceramatec Zeolites, Coal fly ash and 13X

Zeolite / Fly ash / Support	CEC (meq/g)	
	Pre- Ion Exchange	Post Ion Exchange with (K+)
Ceramalite C71	3.01	3.13
Ceramalite C11	2.50	2.65
DELTA	<0.038	0.15
MRTF	<0.05	< 0.07
EWB	0.03	< 0.07
13X	2.70	3.31

Task A-1.4, A-2.4, and A-3.4 Characterization of Ion-exchanged Materials

Aside from characterizing the ion-exchanged materials via CEC, we also used chemical composition analysis to detect the presence of K⁺ in the post ion-exchanged material structure. For this we used a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS), which is a semi-quantitative technique to determine relative ratios of specific elements of interest. For these experiments we determined the

elemental content of Si, Al, Na, O, and K using EDS. The presence of potassium was confirmed by EDS, and the results are shown in Table 4.

Table 4. Relative metal ion composition of K⁺ exchanged Zeolites, Fly ash and 13 X using EDS.

Zeolite / Fly ash / Support	Wt. % Na	Wt. % Al	Wt. %Si	Wt. %O	Wt. %Cation (K ⁺)
K+ Ceramalite C71	5.03	15.45	20.4	50.13	8.99
K+ Ceramalite C11	2.39	15.08	25.69	50.88	5.96
K+ DELTA	2.97	14.25	32.63	48.39	1.75
K+ MRTF	2.85	11.47	22.62	62.34	0.72
K+ EWB	1.52	34.54	24.4	34.73	4.81
K+ 13X	5.89	14.93	23.34	48.01	7.83

Application 2: Heavy metal ion exchange (One way exchange)

The second application was performed to evaluate our synthesized zeolite materials as prospective adsorbents for waste water treatment applications. Waste water treatment is one of the most common applications for the use of zeolites. This is because of the high capacity for adsorption of heavy metals that cannot be discharged to the environment. The heavy metals of interest to us initially are Fe, Co, Ni, and Cu. Each of these metal ions were incorporated into the zeolite structure using the corresponding metal ion nitrate solution via the ion exchange procedure outlined in Table 5. The experimental metal ion concentration in DI water was maintained at 100 ppm, which is close to the observed value for most wastewater streams. In the first set of experiments commercial 13X zeolite was used to establish baseline reference for Ceramatec zeolites that are to be tested in near future.

Table 5. Procedure for Heavy metal ion exchange

Step 1: A 100 ppm salt solution containing heavy metal Fe 3+, Co²⁺, Cu²⁺, Ni²⁺ is prepared using DI water

Step 2: To 1 g of 13X/zeolite /hierarchical zeolite /fly ash 100 cc solution containing 100 ppm metal is added to a conical flask

Step 3: The solution is stirred for 24 hr at room temperature. The ion exchanged 13X commercial zeolite is recovered by vacuum filtration and dried in oven for 24 hr. at 100°C for analysis.

Characterization

These ion exchanged zeolites are analyzed using EDS. It can be observed that the concentrations of heavy metal ions is too low for EDS detection (Table 6) indicating, alternate analytical technique must be adopted to quantify the ion exchange. This future

work will involve analysis using an Inductively Coupled Plasma Analyzer (ICP) to measure very low concentration of metal ions, both before and after the exchange. Ceramatec's analytical laboratory is equipped with a Perkin-Elmer ICP. We must develop a process for analyzing our zeolites heavy metal adsorption via ICP, because zeolites have not been analyzed in the Ceramatec analytical facility before. Therefore at this point it is unclear how well the zeolites are adsorbing these heavy metal ions.

Table 6. Relative metal ion composition of heavy metal ion exchanged commercial 13X zeolite using Energy dispersive spectroscopy

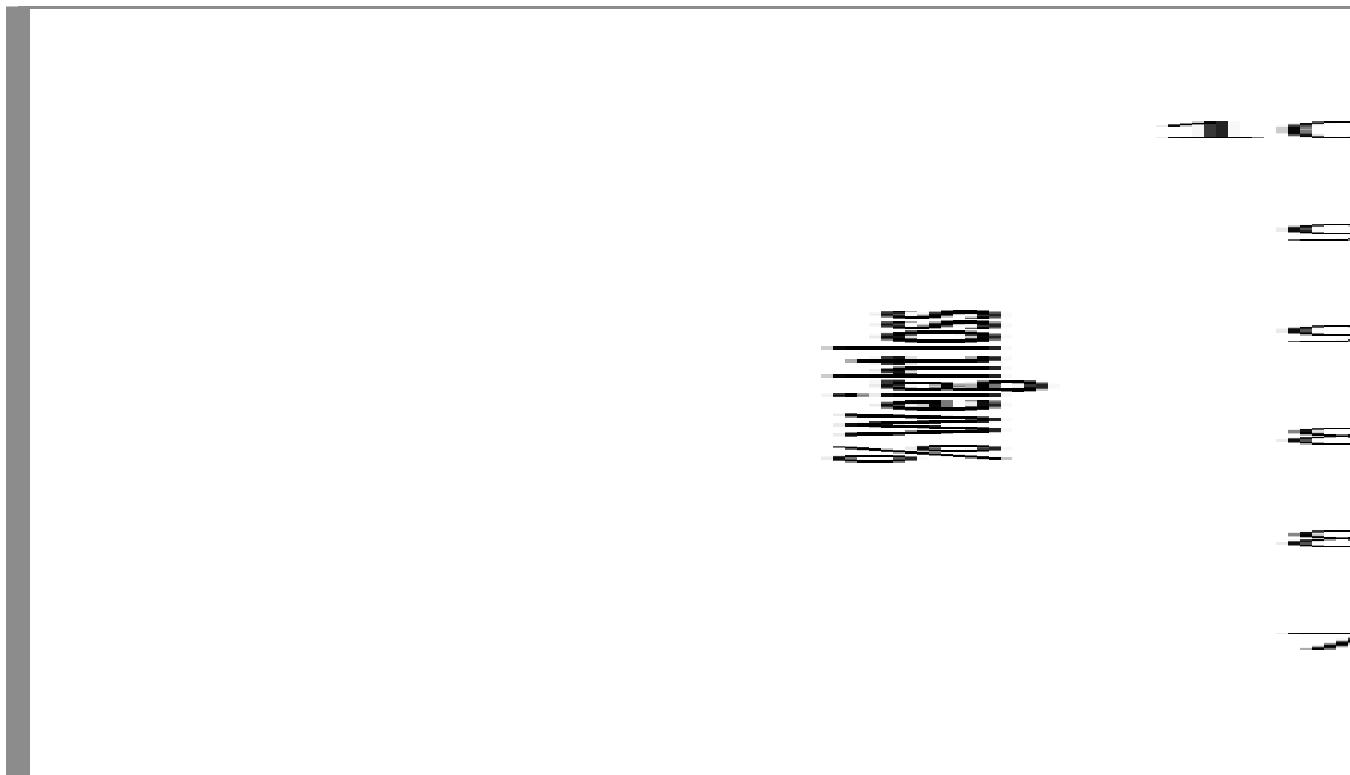
Heavy Metal Ion	Metal Salt	Zeolite	Metal ion Conc. ppm	Weight of zeolite(g)	Wt. % Na	Wt. % Al	Wt. % Si	Wt. % O	Wt. % Heavy metal ion
Fe ³⁺	Fe(NO ₃) ₃ .9H ₂ O	13X	100	1	3.2	11.5	36	49	BDL
Co ²⁺	Co(NO ₃) ₂ .6H ₂ O	13X	100	1	11.7	14.7	22	51	BDL
Cu ²⁺	Cu(NO ₃) ₂ .XH ₂ O	13X	100	1	12	15.8	25.5	46	BDL
Ni ²⁺	Ni(NO ₃) ₂ .6H ₂ O	13X	100	1	8	12.9	30	48.5	BDL

BDL – Below detection limit

Task A-3.1: Hierarchical Zeolite Synthesis: Hierarchical zeolite synthesis was done in a similar manner as described for the synthesis of zeolites from fly ash.

The hierarchical zeolites formed from fly ash are characterized using Thermo gravimetric analysis TGA in the presence of nitrogen and air. The hierarchical zeolite C-71 (Ceramalite) was calcined in air and nitrogen. The weight loss associated with the loss of moisture was determined experimentally. The TGA data were recorded from room temperature up to 700°C. The TGA data yields information on the minimum temperature the zeolite needs to eliminate the pore water for calcination. Figure 1 shows that at 300°C, greater than 20% of the sample weight is lost, which is attributed to moisture loss. Hence the activation temperature of the hierarchical zeolite (HZ) should be greater than or equal to 300°C. The TGA also helps us understand whether or not the HZ is stable at high temperatures or not. For the data shown in Figure 1, the hierarchical zeolite C-71 was stable up to 700°C. Most conventional zeolites lose their structural stability at temperatures in excess of 600°C. Thus, it is clear that the Hierarchical zeolites synthesized by Ceramatec are significantly more stable than the commercial zeolites.

Figure 1:TGA analysis of C-71



A-3.4.2 Particle size analysis (PSA)

The fly ash based hierarchical zeolite C-71 was analyzed for its particle size using a particle size analyzer with water and propanol as the different solvents (Fraunhofer method). The average particle size of the Ceramatec HZ was about 3.6-5.7 microns as given in Table 7.

Table 7 Particle size analysis (PSA)

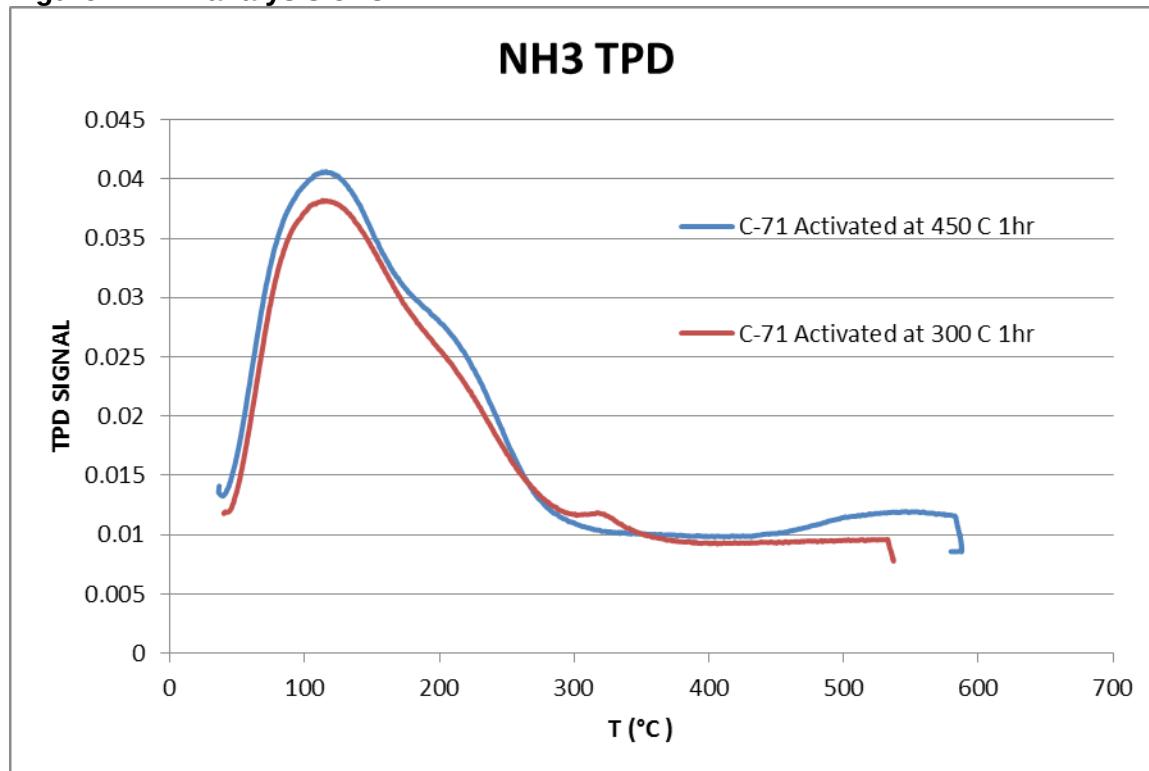
Sample	Mean	D10 (μ m)	D50 (μ m)	D90 (μ m)	Comments
C-71	3.652	1.335	2.922	6.723	Water
C-71	5.796	1.642	4.386	11.610	2-Propanol Fraunhofer

A-3.4.3 Temperature programmed desorption (TPD)

The measured acidity of zeolites plays an important role in determining the nature and feasibility of catalytic reactions carried out using that particular zeolite material. Therefore, Ceramatec characterized the acidity of the hierarchical zeolite C-71, and it was analyzed using NH₃-TPD. The C-71 sample was first “activated” at 300°C and

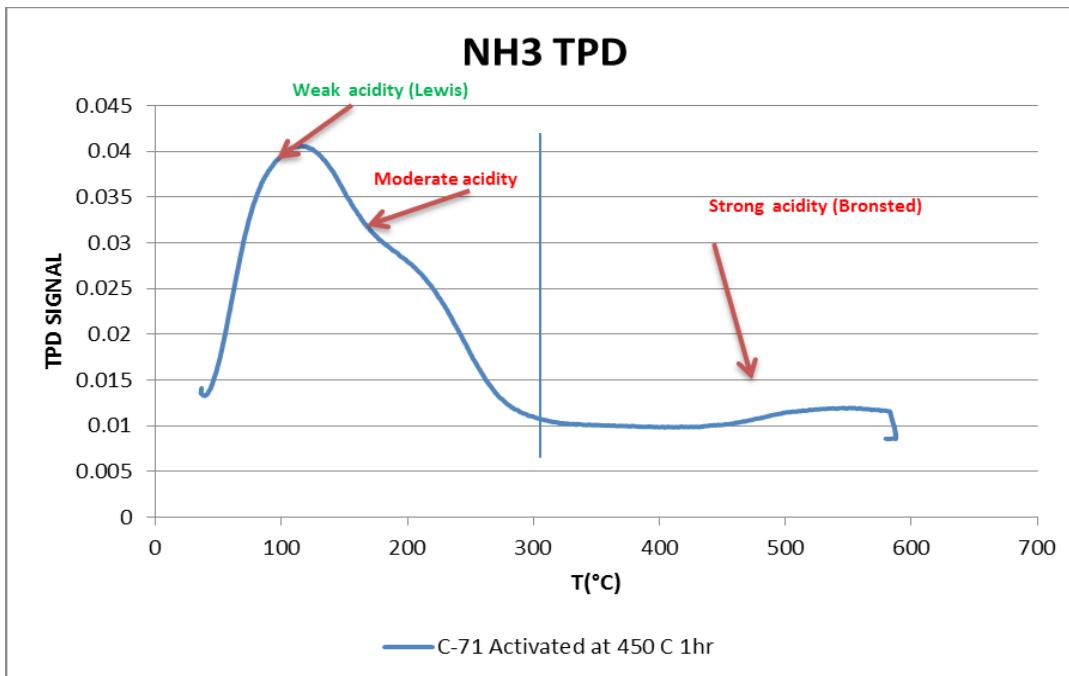
450°C for 1 hour (in helium) to ensure removal of any surface water. Figure 2 shows that higher activation temperatures, of 450C, yielded better results with which to understand the surface characteristics of the zeolite.

Figure 2. TPD analysis of C-71



The activated sample was saturated with NH₃ to occupy the acidic sites in the HZ. The HZ sample was then exposed to increasing temperature, from room temperature to 600°C, in order to observe the NH₃ desorption process. Since the NH₃ molecule occupies the acidic sites in the zeolite, the amount of NH₃ desorbed is indicative of the number of acid sites, i.e. the “acidity” of the material. Furthermore, the nature of the acidic site, e.g. weak, strong, etc., may also be determined from this data. Weak acid sites are characterized by low desorption temperatures. For the Ceramalite sample shown in Figure 3, a large peak occurs at about 120°C. This peak for NH₃ desorption indicates a strong presence of weak acidic sites. At 200°C, a small shoulder in the peak is characteristic of “moderate acidity” sites. Lastly, the peak at 500°C indicates the presence of strong acid sites. The C-71 sample is hence composed of weak to moderate acidic sites, which are favorable for dehydration reactions, but not cracking reactions, which require the presence of strong acid sites.

Figure 3 Acidity of C-71



The characterization of these materials is critical for determining their potential applications as improved zeolite structures. We will continue to analyze these materials from each batch that is prepared, and include the data in our main database. Any new process variations for the synthesis of these materials will be characterized using these techniques described above to quantify the process parameter changes effects on overall sample properties. The characterization and synthesis of these materials has been completed, and we are now focusing entirely on the application of these novel materials.

Task B: Adsorption-Desorption Testing

Task B-1: Experimental Test Design and Setup

The experimental setup for this task is shown in Figure 4. This setup was built for the testing of Ceramatec's zeolites, hierarchical zeolites, and various commercial zeolites for several adsorption applications. All parts and equipment were purchased and installed for this setup. Task B-1 is now complete.

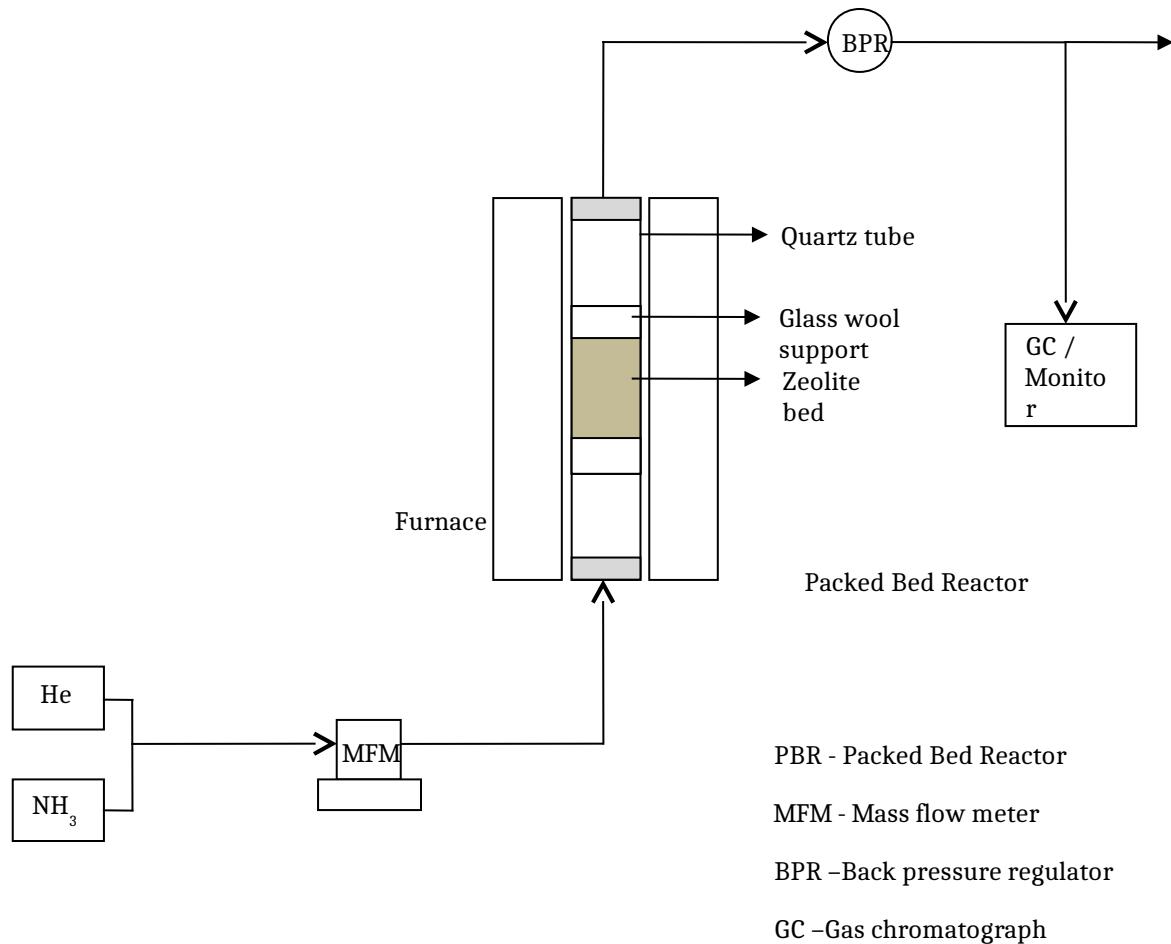


Figure 4. Adsorption test setup

The test gas (CO_2 or NH_3) is mixed with an inert gas (He or N_2) as balance. The flow rates are controlled using mass flow controllers. The feed stream containing a known amount of adsorbate is passed through the adsorber containing the packed bed of zeolites (diameter of particle 100-180 μm). The bed is supported using glass wool on either side. The reactor size chosen was $\frac{3}{4}$ inch (to avoid Channeling D/D_p : 20-50 (D -reactor diameter, D_p diameter of particle)). The adsorption can be enabled at higher pressures using a back pressure regulator. The outlet gas is monitored using a Varian micro GC and a gas monitor (RAE-systems). In order to regenerate the bed, a thermal swing desorption process was adopted (assisted by the furnace).

Task B-2: Adsorption – Desorption Testing:

The experimental setup enabled testing of Ceramatec's proprietary zeolites (Ceramalites) for NH_3 , CO_2 sorption and CO_2 conversion. Testing included the following.

- **Adsorption cycle:** the adsorption is facilitated by physisorption, which is a physical adherence of the adsorbate molecule on the surface of adsorbent because of van-der-waal forces of attraction.

- Desorption cycle: the adsorbent bed will be regenerated using thermal swing (TSA)/Pressure swing (PSA) or thermally assisted PSA (PTSA) processes.
- Estimation of Sorbent Capacity: (cc/g) capacity is calculated using breakthrough plots generated during adsorption: C/C_0 vs. t (C : outlet concentration, C_0 inlet gas concentration).
- Capacity vs. Number of cycles: the adsorbent bed will be tested for the loss of adsorption capacity for multiple adsorption-desorption cycles (e.g. 50-200 cycles)
Thermal Stability: the adsorbents will be tested for their structural stability and integrity at elevated bed temperatures (for example: 600°C, 700°C, 800°C).

All catalyst and zeolite testing is described in Task E below.

Task C: Incorporation of Zeolites with Animal Litters

1. Actual Accomplishments:

Task C-1 Design Mixing Process for Combining Animal Litter with Zeolites: We have investigated several methods for incorporating zeolites into animal litter materials for enhanced odor control. Commercial zeolites are available for purchase in a multitude of mesh sizes, and are available in greater quantities than zeolites made using our synthetic process. Therefore, for these bench-top baseline studies we began by utilizing the commercial materials in order to preserve our synthetic materials for other testing. A simple way (known hereafter as Method 1) to incorporate zeolites into our fly ash animal litter is by *physically mixing* zeolites of an appropriate mesh size into the litter at a defined ratio. For example, commercial zeolite 13X can be purchased as a 1.6mm pellet, sized to a 40/60 or a 60/80 mesh (U.S. standard sieve sizes). This size is ideal for combining with various animal litters without disrupting the preferred litter granule size distribution or creating unnecessary dust.

A second mixing process, which may result in a more homogenous mixing of zeolites than Method 1, is done by incorporating zeolites with each individual animal litter granule. If each granule has some zeolitic characteristics, it may be possible to use less zeolite material and achieve the same odor eliminating results. This mixing can be accomplished by starting with zeolite powders. These powders would be best if they are passed through a size 100 mesh, although a powder that passes through a 200 mesh would be most preferred. This zeolite powder could be incorporated in one of several ways.

One way to incorporate zeolite powder into an animal litter is to include it in the initial batching steps (Method 2). Although this ensures the greatest homogeneity, this method is not preferred because some of the zeolite would not be accessible to capture ammonia as it may be trapped *within* the fly ash litter granule. This method was not attempted in any subsequent tasks because of the low probability of success.

Another, more-preferred method (Method 3), is to create a zeolite coating on the exterior of the animal litter granules. This particular method is preferred simply because the entire amount of zeolites added to the litter batch are now easily accessible (i.e. on the outer surface of the litter particle) for odor control. For large-scale synthesis of Method 3, we envision applying the zeolite coating by using a rotating drum. Wherein, moist animal

litter granules are fed into the rotating drum while the dry zeolite powder is sprayed evenly on the surface of the particles. This is a powder coating method, because the zeolite powders are dry. The moisture of the litter granules will act as a binder for the zeolite, which is coated by the dry zeolite powder.

The fourth and final method envisaged, is spraying suspended zeolite powders (in solution) to dry granules. Water may not be a strong enough binder and one might have to worry about the attrition of zeolites from the surface of the granules. To solve this problem, the use of an additional chemical binder might be necessary. This is Method 4.

In summary of Task C-1, we have completed our preliminary analysis of designing the mixing process for incorporation of zeolites with animal litters. Task C-1 is complete.

Task C-2 Combine Zeolites with Commercial Animal Litter: The original intent of this task was to potentially improve the odor control capabilities of commercial litter products. This could be accomplished by combining either commercially-available zeolites or synthetic zeolites made by Ceramatec into the commercial litter product. However, given the lack of interest from commercial litter manufacturers in having Ceramatec improve their litter materials, we have not performed any work on this Task. Furthermore, we do not anticipate adding any zeolites to commercial litters in the future in order to keep our R&D focus on the Ceramatec manufactured litter products. Therefore, we consider this Task to be complete.

Task C-3 Combine Zeolites with Ceramatec Fly Ash Litter: Several of the zeolite incorporation methods discussed in Task C-1 were employed in the execution of this task. For this task, zeolites were incorporated into a Ceramatec animal litter by dry mixing appropriately sized 13X with the litter (i.e. Method 1). Zeolite 13X was mixed at a 1 wt%, 5 wt%, and a 10 wt% addition, based on the total weight of litter (including the added 13X). This dry mix method of incorporating zeolites into the Ceramatec animal litter is preferred for its simplicity; however, as mentioned the uniformity of zeolite distribution may not be ideal.

The next method employed was suspending zeolites in solution and then mixing this solution with dry animal litter granules (Method 4). A 5% solution of zeolite 13X was prepared and applied to the animal litter in a ratio that was equivalent to a 1 wt% addition of zeolite, based on the weight of the total litter. Once dry, the coated granules were passed through a number 12 sieve and retained by a number 50 sieve.

Finally, we incorporated zeolites using a powder coating method (i.e. Method 3). Zeolite 13X in the form of 1.6mm pellets were ground using a hand mill and the ground material was passed through a number 140 sieve and collected. Until a manufacturing size scale up is possible, a laboratory simulation of the powder coating method previously outlined in Task C-1 was necessary, and was tested as follows. A standard spray bottle of DI water was used to mist the animal litter granules until they appeared damp. The minus 140 mesh powder was applied to moist animal litter granules by sprinkling until a light dusting was achieved. At this point, we simulated a rotating drum by physically mixing the material until it appeared dry again. The misting and dusting procedure was repeated until a 5 wt% addition of zeolite powder was complete. Once dry, the material was again sized to a -12, +50 mesh. While sieving the zeolite powder coated animal litter, we observed a high attrition rate.

The applied zeolite incorporation methods discussed in Task C-3 were tested for their odor controlling abilities. A standard method for testing a litter's ability to control odor was developed. From our visit to an independent animal litter distributor, we learned that most litter testing facilities use a solution of 10-15% household ammonia in order to recreate the smell associated with the degradation of animal urine. This solution is used to test the odor eliminating capabilities of an animal litter. Most household ammonia solutions are suitable for use in animal litter performance testing.

The procedure for the odor test is as follows. Ten milliliters of the previously referenced ammonia solution is poured onto 50g of the animal litter in question. A timer is started. At one minute and at one hour the animal litter is "smelled" and the odor is ranked as follows.

- 1 – Very strong odor
- 2 – Strong odor
- 3 – Weak odor
- 4 – Very weak odor
- 5 – No odor

The animal litter is given a total score based on its performance at one minute and at one hour. In order to compensate for the subjective nature of this ranking system at least two people are involved in the scoring of the litter performance. Other quantitative ammonia detection methods were researched for use in odor testing but the human nose is generally much more sensitive than the most advanced ammonia detecting equipment. The results of our testing for animal litters made by Ceramatec and with zeolite 13X additions are included below in Table 8.

Table 8: Odor test results for zeolite incorporation methods

Zeolite Incorporation Method	%wt	1 min	1 hour	Total
13X Suspension (Method 4)	1	1	3	4
13X Dry Mix (Method 1)	1	1	4	5
13X Dry Mix (Method 1)	5	1	4	5
13X Dry Mix (Method 1)	10	2	3	5
13X Powder Coating (Method 3)	5	2	3	5

The addition of zeolites has good odor control characteristics at the 1-hour timeframe; however, they are quite poor for odor control at 1 minute. Qualification testing for product acceptance requires good odor control characteristics at both time intervals. Therefore, we must continue to study how to improve the 1-minute odor control scores to a level that will be acceptable.

Section C would more appropriately be titled "Incorporation of Odor Control with Animal Litters". Through initial odor trials using zeolites, it became apparent that using zeolites alone would not be sufficient to control odor in animal litter. A combination of pH buffers,

urease inhibitors, perfumes, and absorptive materials, like zeolites, will be necessary. To this end, we have extended the range of work associated with this task to include studying odor control capabilities of not only the Ceramatec animal litters, but also the commercially-available animal litters as well for comparison of our results. As described above, we have developed an internal method for testing the odor control of various animal litters. Despite the subjective nature of the testing itself, this appears to be an industry standard practice, as determined from site visits to an animal litter test facility in Phoenix, AZ.

For comparison purposes, several types of commercial animal litters were tested as described above. Their results of these tests are given in Table 9.

Table 9: Odor test results for commercial litters

	Commercial Litter	1 min	1 hour	Total
Clumping	Arm & Hammer Super Scoop	4	5	9
	Tidy Cats Scoop	4	5	9
	Fresh Step	1	3	4
	Scoop Away	2	4	6
	Litter Perfect	3	4	7
	Cats Pride Scoopable	4	4	8
Non-Clumping	Tidy Cats Clay	4	5	9
	Jonny Cat	1	4	5
	ExquisiCat Premium White	3	4	7
	ExquisiCat Crystals	4	5	9
Naturals/Hybrids	Feline Pine	4	5	9
	Swheat Scoop	1	4	5
	Fresh Aire Cedar Additive	3	5	8
	Fresh Aire with Bio Filters	1	5	6
	World's Best	4	5	9
	ExquisiCat Paper	3	4	7

The average score for commercial litters at one minute was 3, the one hour average was 4, and total score average was 7. In conclusion, in order to perform on par with commercial animal litters, our product should work quickly to control odor with little to no ammonia odor remaining after 1 hour. Referring back to Table 8, it can be seen that simply adding zeolite 13X yields an average score of ~5, which is significantly lower than the commercial litters average score of 7. This further confirms that improvements to the odor control capability of our litter products must be improved.

In the past year, we tested approximately 20 different types of potential odor controlling agents. The deodorizers tested were an assortment of pH buffers, urease inhibitors (odor causing ammonia is generally due to the breakdown of urea by the enzyme urease), and absorbent materials. The pH buffers work to neutralize the odors caused by ammonia. Below a pH of 7, ammonia will exist as an ammonium ion which does not cause the noxious odor associated with volatile ammonia gas. Urease inhibitors will slow

the decomposition of urea by blocking the enzymatic breakdown of urea into ammonia. This delays the production of ammonia odor from animal urine.

The two most successful deodorizing agents employed in the animal litter were boric acid and citric acid. These are weak acids which act to neutralize volatile ammonia. Boric acid is preferred to citric acid because it also serves as a urease inhibitor. Boric acid was tested in its powder and crystalline form. Crystalline boric acid is favorable because it does not add dust to the animal litter. After multiple odor tests using a 5 wt% addition of boric acid crystals, the animal litter averaged scores of 3, 4, and 7 for one minute, one hour, and total score respectively. These scores are comparable to the commercial litters tested.

Task C-4 Characterize Combined Materials: We have harnessed a great deal of knowledge about the odor causing elements associated with cat dross and how these can be controlled. Volatile ammonia is the leading component in odor from cat excretions. Urea, a constituent of cat urine, is broken down by the enzyme urease into ammonia by the following reaction.



Urease is one of the most prevalent enzymes in the world and is generally found in bacteria. In order to compete with commercial litter odor control technology, we have decided to take a three-fold approach to odor control: neutralize, capture, and inhibit.

First we will neutralize ammonia as it evolves. Ammonia gas (NH_3) volatilizes at pH 7 and above. Below this pH, it exists as the ammonium ion (NH_4^+) which has no associated odor. We will neutralize ammonia gas with a weak acid, causing it to be converted into ammonium and no longer contributing to odor. The second phase is to capture the ammonia within the pore structure of absorbent materials. Ammonia exists in trace amounts in urine; it is a very soluble gas. We can capture any solubilized ammonia by absorbing the urine with an absorbent material. Preferably, we will use a highly porous material like a zeolite or a desiccant. By quickly capturing moisture, we also help slow the hydrolysis of urea to ammonia via the above reaction. The third stage of odor control is to inhibit the urease enzyme, slowing the evolution of ammonia. This can be done with urease inhibitors or antibacterial agents. In addition, the optimum pH range at which urease functions is 7-10. The weak acids from phase one will aid in urease inhibition.

In Q4 FY10, we designed and tested different methods for the incorporation of odor control agents into our animal litter. At this point, we have decided that a physical mixing of the dry materials is the most appropriate method for our initial odor testing. A few of the other previously discussed mixing techniques have been attempted with different odor control agents and have had intermittent success at best. Once we have selected our most favorable odor control agents and begun the scale-up process, these mixing methods can be revisited.

We have focused our attention and resources on developing two types of animal litter: a non-clumping recycled litter and a clumping litter. Both litters integrate (and require) odor

control and “Reasons-to-Believe” (RTB), so these will be discussed in this section. Advances in the Ceramatec clumping litter will be discussed under Task D. For manufacturing simplicity, we plan to use identical odor control technology and RTB in both types of litter. All odor control tests were performed the same as outlined in the previous quarter’s report.

We discovered that a 5 weight percent addition of boric acid was sufficient for odor control. These tests were executed by mixing the boric acid with a Ceramatec litter made from fly ash code named MGW0908. We have moved away from using this fly ash as starting material because of its darker color. Most cat owners prefer a tan or white colored cat litter because it does not track across light colored carpets. Instead we have begun to use fly ash MRT1010 or SEP1010. These produce a light tan colored litter (see images in Figure 5 below).



Figure 5. SEP1010

MRT1010

MGW0908

Although they produce a lighter colored litter, they require more than the 5wt% boric acid to score on par with commercial litters for odor control. The MRT litter with a 5wt% boric acid addition only scores a 1 and 3.5 at the one minute and one hour mark respectively (recall that a score of 1 = strong odor, and a 5 = no odor). In order to compete with commercial litters, we have set a goal of a score of at least 2 at one minute and 4 at the one hour test. Adding a scent to the boric acid crystals improves scores to 1.5 and 5 but many cat owners prefer an unscented litter option so we cannot depend on scent to improve odor control. In addition, boric acid alone does not employ our 3-fold odor control approach.

In this quarter, we have tested weak acids, zeolites, desiccants, and combinations thereof in order to optimize our odor control. Weak acids and absorbents were selected for their low cost and nontoxic nature. We have tested ten weak acids and ten absorbents in varying weight percent additions and combinations. Examples of weak acids tested include but are not limited to: boric acid, citric acid, terephthalic acid, lauric acid, etc. Absorbents tested include but are not limited to: Zeolites 13X, ZSM, Sodium Y, Ammonium Y, Clinoptilolite, activated alumina, and silica gel.

“Reasons-to-Believe” are the flecks of color you find in commercial litter products. These indicate to the consumer that the litter employs some sort of odor control technology and comes in an array of colors. Ironically, they actually do nothing to improve odor control

and are usually just litter granules with a thin coat of paint. It is the appearance of odor control that is the most important element of RTB. Originally, a soy-based concrete stain was selected for our RTB with light blue being the color that worked best on all our fly ash sources. Although these soy-stain RTB accomplished their intent, they gave off a slight paint-like odor which actually lowered our odor control scores. This is the reason we began to incorporate silica gel into our litters. It can be purchased in an assortment of colors, blue is preferred, and works well as an absorbent and for RTB. Below in Figure 6 are two images of litter with blue soy stained RTB and silica gel RTB.



Figure 6. Soy RTB Silica Gel RTB

Task D: Litter Performance Testing

1. Actual Accomplishments:

Task D-1: Independent Lab Testing of Odor Control:

Task D-2: Internal Clumpability Testing: We have performed internal clump testing of our materials to a significant degree. Creating a clumpable animal litter is of critical importance to the success of this product (with respect to consumer acceptance). Several generations of clumping technology has been studied during the past fiscal year. Task D-4, Process Optimization, contains a description of the most recent results of the latest internal clump testing. These results were generated using our latest technology for clumping.

Task D-3: Independent Lab Testing of Clumpability: As a result of potential investor interest in our litter product, we began to focus more acutely on the development of our Ceramatec animal litter and its performance testing. Task D-3, intended for Q3 FY11 of this project management plan, was initiated during this past fiscal year FY10. To that end, our team visited an independent distributor of animal litters and brought several samples of our product for clumpability testing.

The animal litter distributor educated us on the four major categories of cat litter. These are outlined below.

1. *Non-clumping clay*: Characterized by a non-clumping absorbent material, usually a type of absorbent clay. Consumers judge this product by its appealing color and its

ability to control odor. This category is very price sensitive as it is the most basic animal litter and least expensive to produce.

2. *Clumping clay*: This is most often a litter made of clumping sodium bentonite clay. Sometimes it is a blend of sodium bentonite and another type of clay in order to reduce cost and bulk density. The consumer of this product expects it to eliminate odor and clump on contact. This is currently the majority of the cat litter market.
3. *Solution seekers*: These are litters produced for cats with special needs. They are the most expensive and usually address some medical need.
4. *Naturals*: This growing market is characterized by litters made of natural or recycled materials. Examples include corn, wheat, recycled paper, pine, etc. These products are expected to eliminate odors. Some are clumping litters while others do not clump.

Sub-categories are beginning to emerge that combine the distinctions of the above groups. Ceramatec is performing R&D to develop three products: a non-clumping litter; a hybrid litter composed of sodium bentonite and fifty percent or more recycled fly ash litter; and a clumping litter made from recycled material with no clay additive. All three will have odor controlling elements. The hybrid will use sodium bentonite as its clumping agent and the clumping litter will use an alternative, natural clumping agent.

Results of the Independent Lab Test #1: A 5-lb sample of kitty litter made using fly ash in our lab was delivered to the independent testing lab. This sample had a clumping agent added to the litter. Our in-house testing showed that this clumping additive performed well, and passed our internal testing criteria. In addition to sending the samples, we visited the testing facility during the testing to learn exactly how this facility conducted its experiments to quantify clumpability. This was an extremely educational visit, simply because their tests were conducted very crudely, and our testing procedure was not adequate.

From their testing, we determined that our original clumping agent formulations were not strong enough to pass the independent testing facility's standards. A clumping litter is expected to withstand rough scooping at as little as one minute after being wetted. The resultant clump should be stable enough to be picked up *by hand* and handled with no crumbling or breaking within the first minute! We knew that our clumping agents would require more than one minute to set up and stabilize because we did all of our testing at the 5-minute point. In short, the conclusions of the independent lab testing of our clumpable kitty litter were not good. We failed with regard to 1-minute clump testing, and we also failed their clump tests at the 1-hour timeframe. Typically the independent lab also performs 2-day clump testing, but given the initial results, no 2-day clump tests were conducted on this initial visit. The poor report on our initial attempts at a clumping animal litter caused us to return to clumping agent development, and we adjusted our internal clumpability testing to better reflect industry practice.

Results of the Independent Lab Test #2: Task D-4 is process optimization, which we conducted during Q4FY10. The result of our optimization was an improved clumpable litter, which was sent to the independent testing facility for clump testing. The descriptions of the changes made to this litter are described in Task D-4.

The material sent to the lab for additional testing was a "hybrid" animal litter consisting of 50% sodium bentonite clay and 50% Ceramatec litter. From our testing we determined that one of the best clumping additives was in fact bentonite clay; therefore we

developed a litter that was a mixture of green materials and clay materials. Approximately 5 lbs. of the hybrid litter was sent to the testing facility. An image of the hybrid litter is shown in Figure 7. The results of their evaluation revealed that the initial clumping (measured at 1-minute) was comparable to commercial brand litters, and was rated “superior” by the testing facility. The results of multiple tests revealed excellent clump integrity at the 1-minute mark. This was considerably better than our previous test described above. However, the 50/50 hybrid exhibited poor clump integrity after it had dried (tested after 48 hrs. of drying). Based upon our in-house testing, the 48-hour result was too surprising, because we had observed in the lab intermediate clump integrity at long time intervals. Additional work is now being conducted to increase the long-term clump integrity.

Figure 7: 50/50 “Hybrid” Litter



Task D-4: Process Optimization: Following the visit with the independent testing facility and witnessing their testing methods, we decided to simplify our internal clumping test. Previously, we had made a visual assessment of clumpability at several points after the litter had come in contact with water. Now, the clump is only assessed at one minute, one hour, and when it has dried (~48 hours). The visual assessment of clump integrity is a rank of 0, 1, or 2: a score of 2 is a solid, stable clump; a score of 1 is a clump that

breaks into pieces large enough to be scooped; anything less is a failed clump and results in score of zero. Notes about the integrity of the clump, such as how much it crumbles, are taken at each evaluation point. A clump can only “pass” the test if it scores a 2 at each inspection point.

If a clump passes, another test is administered to determine the clump's ability to withstand stress. The clump is weighed, dropped from a height of 12 inches, and evaluated. It is assigned a number depending on its survival: 1 – does not survive, 2 – breaks into several pieces, 3 – survives with slight crumbling, 4 – clump survives and is stable after drop. If the clump survives the drop, it is weighed again to determine its percent of survival. If the clump broke into pieces, those large enough to be scooped were collected and weighed too.

Our independent lab results forced us to re-design our clumping additives for increased performance. In order to produce a clumping litter made from recycled material, we discovered several materials to act as an ideal clumping agent. Many types of chemicals and combinations thereof were tested as potential clumping agents during this past year. Two in particular caught our special interest because of their ability to swell upon hydration. It is believed that the clumping power of sodium bentonite is because of its ability to swell when it comes in contact with water. This is due to the intercalation of water molecules into the voids between the planes of the bentonite material.

Table 10 shows clumping scores and drop scores for varying %wt additions of clumping additive #1.

%wt	1 min	1 hour	48-hr	Clump Total	Hardness	% Survival
0.5	1	1	2	4	N/A	N/A
0.5	1	2	2	5	N/A	N/A
0.5	2	2	2	6	4	99
1	2	2	2	6	4	96
1	2	2	2	6	4	99
1	1	2	2	5	N/A	N/A
0.5	2	2	2	6	2	90
0.5	1	2	2	5	N/A	N/A
0.5	2	2	2	6	1	0
1	2	2	2	6	3	96
1	2	2	2	6	4	97
1	1	2	2	5	N/A	N/A
2	2	2	2	6	4	96
2	2	2	2	6	4	98
2	2	2	2	6	4	97
3	2	2	2	6	4	96
3	2	2	2	6	3.5	94
3	2	2	2	6	4	97

At as little as 2 wt% addition, this additive consistently performs well on our clump tests and receives high % survival scores. Currently, this additive is sprinkled into the animal litter as a powder. This does cause a slight increase in the measured dust in the final product. Alternative application methods will be employed in order to reduce this side-effect.

The second additive was passed through a number 30 sieve (U.S. Standard Sieve Size) before addition to the litter product. The larger particle size requires a higher weight % addition, relative to additive #1, but it also minimizes the amount of dust in the final product. Below is a table of clump test results for additive #2. This additive consistently passes clumpability standards and is marked by high percent survival scores.

Table 11: Additive #2 clump and drop scores

%wt	1 min	1 hour	Dry	Clump Total	Hardness	% Survival
10	2	2	2	6	4	97
10	2	2	2	6	4	98
10	2	2	2	6	4	98
10	2	2	2	6	4	97
10	2	2	2	6	4	96
10	2	2	2	6	4	98
10	2	2	2	6	4	98

Task E: Alternative Application Testing

1. Actual Accomplishments:

Task E-1: Fly Ash as Inert Filler for Rubber Tires: Literature searches for “mineral fillers for tires” revealed several interesting discoveries. Carbon black is the most commonly used reinforcing filler for tires used today. Although tremendous amount of research has been conducted to study the role of additives and fillers in tires over the last century, and substitutes for carbon black are in high demand. Mineral fillers such as silica, kaolin, carbonates, baryates, and whiting have been introduced into the tire industry with modest acceptance. Their clear cost advantages over carbon black are the main drivers for usage the alternative materials. Particular interest has been shown in the use of alumina silicate spheres recovered from fly ash. In fact, aerodynamic classification of fly ash is commercially available under the trade name Plasfill.

Given the volume of work that has been done to utilize fly ash as a mineral filler for tires, and the existence of a current product on the market (Plasfill), Ceramatec has determined that this particular application is of low market interest. Therefore, we do not intend to do any further research on this application beyond the results of the literature search.

Task E-2: Fly Ash for Roofing Granules: Work on producing synthetic roofing granules from fly ash was performed this fiscal year. The primary goals of this portion of the project were to develop a granulated material that had a very high density, and was black in color. These were the two most desirable properties for roofing granules. We spent several months trying to develop roofing granules that were agglomerated from fly ash powders. These batches were made using several fly ash sources, each of which was black in starting color, indicating a high content of carbon in the ash. Each sample batch was agglomerated using a different type of silicate, hydroxide, or a combination thereof, and they were dried in an air oven at 75-100°C to drive off excess water. The resultant granules, sieved to -12, +30, were stable enough to warrant specific gravity testing. Specific gravity, also referred to as relative density, was tested using methods outlined in ASTM standard C128-04a, the Le Chatelier flask method. A roofing granule should have a relative density of 2.60. The fly ash roofing granules made in our labs had specific gravities of 1.91 ± 0.03 , 1.92 ± 0.05 , and 1.819 ± 0.005 . These were the highest scores we could achieve. The granules are not dense enough to pass roofing granule standards. At this time, it does not appear that roofing granules can be made from agglomerated fly ash. Consequently we are discontinuing our work on roofing granules, and we will focus our efforts onto zeolites and animal litter. This task complete.

Task E-3 Fly Ash Catalyst Supports:

The performance of fly ash based zeolite catalyst supports will be tested for CO_2 conversion to methanol, which is a system of significant importance. This task is directly related to Task A, because for this work we will be using the zeolite supports as high surface area materials that can convert CO_2 to methanol.

Challenges in conversion of CO_2 to Methanol:

There are several challenges in commercial production of methanol from CO_2 . The single most important challenge is that of catalyst. The current commercial catalyst,

Cu-Zn-Alumina is optimized for syngas conversion. An active catalyst optimized for CO₂ conversion to methanol needs to be developed. Such an active catalyst can enable advantageous kinetics of methanol formation from CO₂. The catalyst has two significant attributes: metals/promoters and supports.

We have identified the following supports, promoter, active metals and combinations thereof as suitable CO₂ to methanol conversion catalysts:

Table 12. Catalyst support-promoter-active metal listing.

Support (5)	Promoter(7)	Active metal (3)
γ-Al ₂ O ₃	Cerium	Copper
Ceramalite	Manganese	Palladium
Activated Carbon	Iron	Platinum
13 X	Nickel	
Silica	Cobalt	
	Zinc	
	Zirconium	

We have ordered the above supports, promoters and active metal salts. Approximately 100 catalysts will be prepared using conventional incipient wetness (impregnation) technique. The catalyst test plan will include the following tasks

Tasks:

- I. Experimental assembly for catalyst screening
- II. Synthesis and screening of new class of catalysts
- III. Optimization of catalyst preparation using Design of Experiments (DOE)
- IV. Establish intrinsic kinetics of the reaction to aid in scale up

Experimental assembly for catalyst screening (Current work)

The experimental assembly for methanol production tests is shown in Figure 8. The apparatus will constitute a model CO₂ and H₂ cylinder connected to the reactor (SS, 0.5" diameter) through a manually operated ball valve and mass flow controllers to control flow rates of the inlet gases. The outlet line has back pressure regulator which will control the pressure in the gas flow line. The setup is equipped with a gas chromatograph to analyze concentration of various components in reactant and product stream. The parameters of catalyst testing are listed in Table 13.

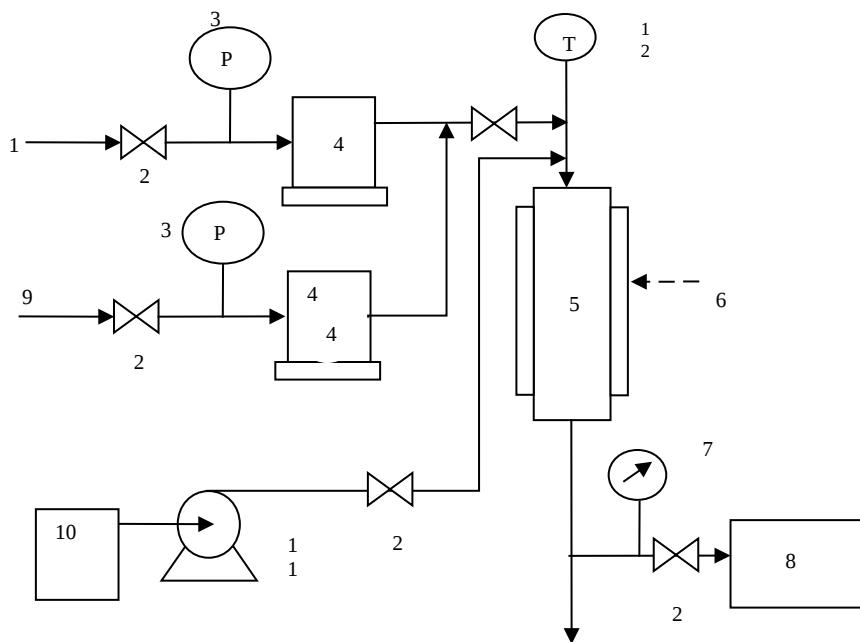


Figure 8. Experimental setup for methanol synthesis

Table 13. Catalyst testing parameters

Pressure:	1 – 10 MPa
H₂ to CO₂ ratio:	2:1, 3:1, 4:1,
Temperature:	175 – 300 °C
Catalyst loading:	1 g, 2 g, 5 g

About 200 different catalysts are anticipated to be prepared using three components: 1) an active metal, 2) a promoter, and 3) a catalyst support. The various materials for selection are outlined in Table 1 below. The combination of these three materials (support-promoter-active metals) were chosen to enable testing for CO₂ conversion to methanol.

Table 14 Catalyst support-promoter-active metal listing

Support (10)	Promoter(7)	Active metal (3)
γ-Al ₂ O ₃	Cerium	Copper
Ceramalite	Manganese	Nickel
Activated Carbon	Iron	
13 X	Nickel	
Silica	Cobalt	
3A	Zinc	
4A	Zirconium	
5A		

ZSM-5		
Zeolite Y		

In last quarter's report, we outlined the method of preparation for the catalysts that were to be tested for CO_2 conversion to methanol or other useful products. The Following is an example recipe previously outlined: **Cu (12%)-Zn (15%)- Al_2O_3**

The conversion of CO_2 to methanol follows the generalized equations listed below:

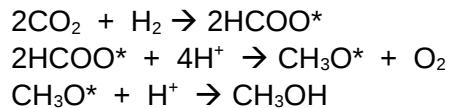
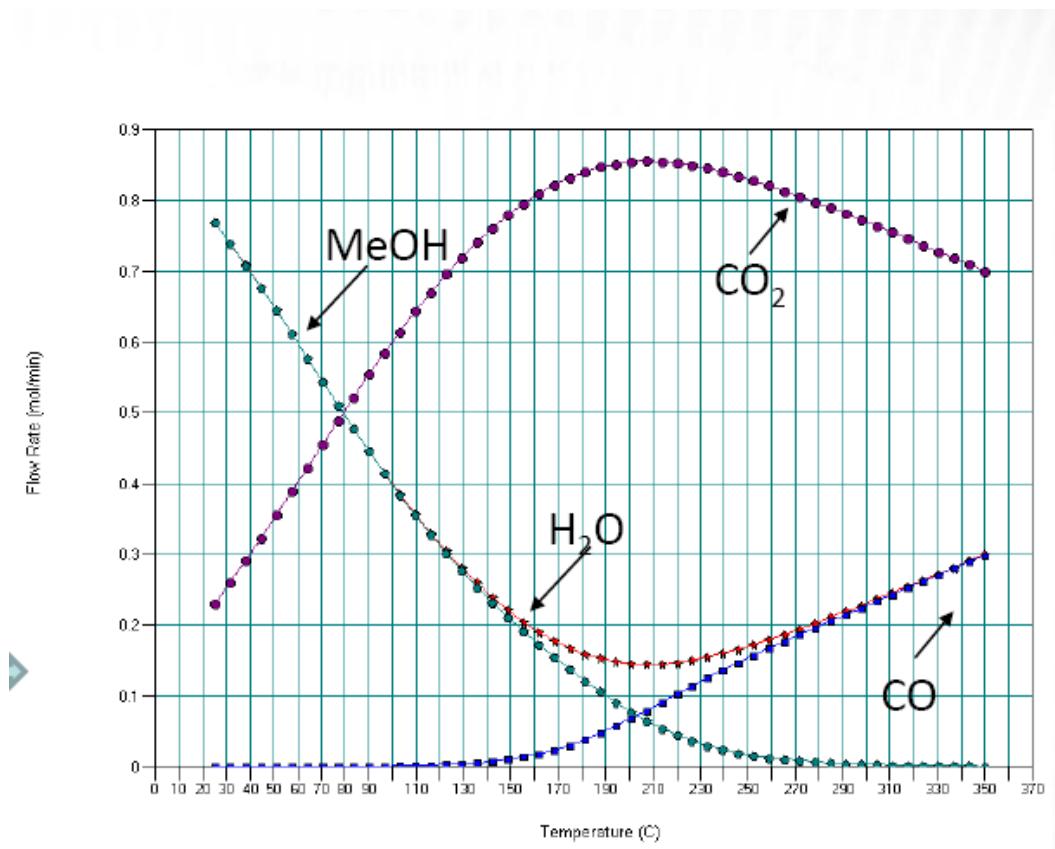
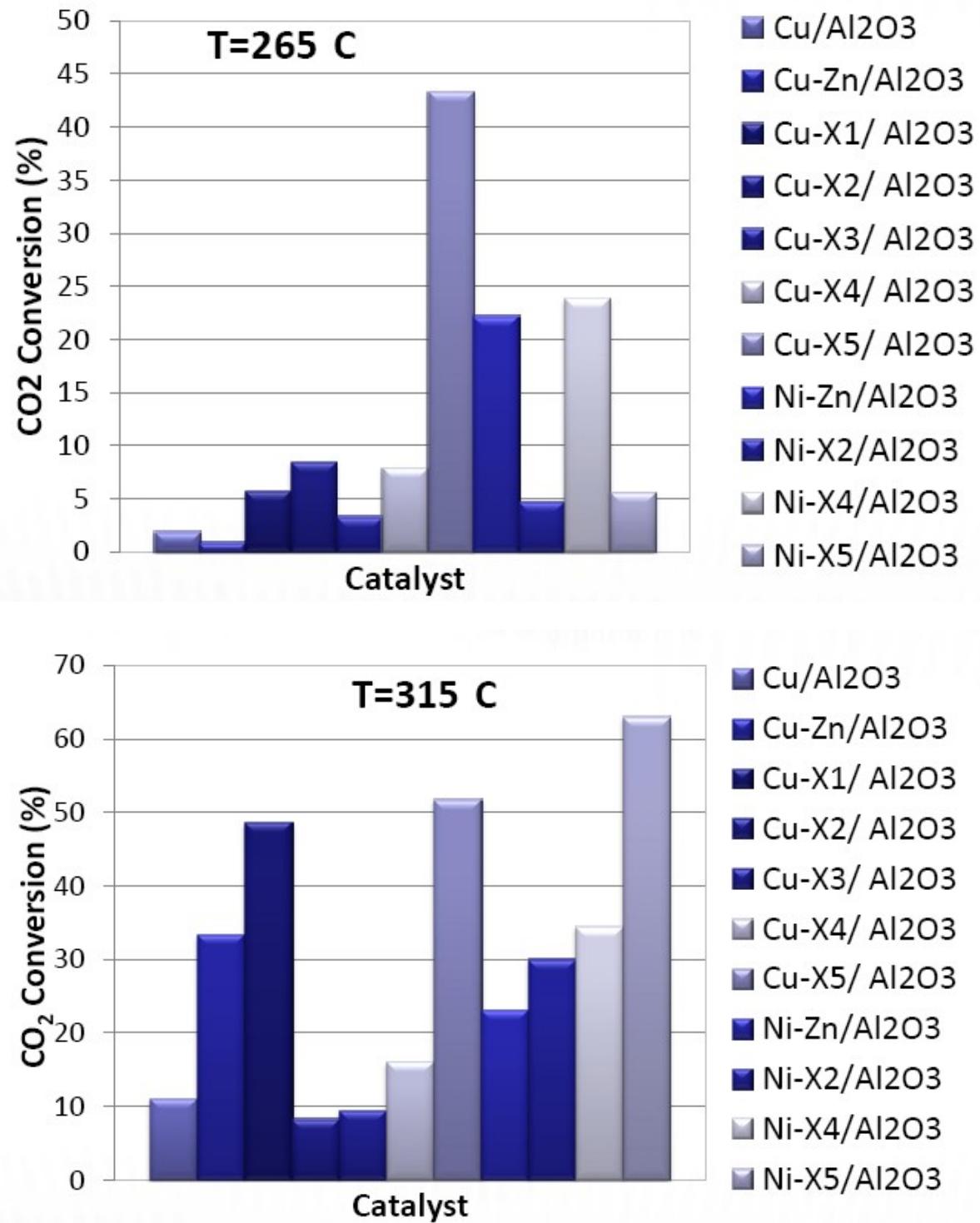


Figure 9 shows a plot of flow rate vs. temperature for several of the products formed from the reaction of CO_2 at a catalyst site. It can be seen from this plot that the formation of CO is also a possible byproduct, and it competes directly with methanol formation from CO_2 . Therefore selectivity of the catalyst combination chosen is a critical factor in catalyst design.



The testing of many of the catalyst combinations outlined in Table 14 began during Q2 FY11. Two temperatures were selected for the reaction described above, 265C and 315C. The results of several catalyst combinations are shown in Figure 3 for 265C, and also for 315C in Figure 10.



Each of the Figures above show the percent conversion of CO₂ to products such as methanol, water, methane, or carbon monoxide. Product detection was quantified by gas chromatography. As can be seen from the data there are several compositions of catalyst that yield greater than 60% conversion of CO₂ with an inlet temperature of 315C. As expected the conversion efficiencies are lower (highest is ~45%) with a lower inlet temperature. Testing is ongoing for all of the catalysts that have been synthesized in our labs. We anticipate testing will continue for the next several quarters, as we determine the best combinations of materials for achieving the highest conversion efficiencies.

Task E-4 Fly Ash Supports for CO₂ Capture: Two high surface area zeolite materials made from two unique sources of fly ash were sent to Los Alamos National Lab (LANL) for testing of their CO₂ capture capacity. Dr. Rico del Sesto and Dr. Michael Janicke are two leading researchers at LANL, and they have agreed to determine the baseline CO₂ capture capacity of the two materials that were sent. The physical properties of these materials were characterized at Ceramatec prior to be sent to LANL. No feedback or data has been provided by LANL to Ceramatec regarding these materials.

Task E-5 Fly Ash for Mineral Fillers for Plastics: No work was ever performed for this task.

Task E-6 Down-Selection of Most Promising Alternative Applications: The litter application dominated our efforts, and therefore very little attention was given to the application of these materials to anything other than conversion to litter or to zeolites.

Task F: Process Scale-Up for Manufacture

Actual Accomplishments: The study of the process for scale-up was very involved and detailed. Moving from hand-made litter to a more robust process was required to determine the feasibility of establishing this as a true manufacturing process. Therefore, we studied several factors affecting the pelletization process that influence the properties of the pellets formed. These factors include drum rotation speed, drum angle, water content of activator solution, fly ash content, desired particle size, desired particle size distribution, etc. We performed several Taguchi Design of Experiments to determine the optimal settings for animal litter formation. Several types of fly ash were used from two different coal fired power plants. The differences between the types of ash used were minimal. The pelletizer has increased our production rate of the litter material from a few kg's per week to 2 kg/hour, and there is still significant room for growth of this process. Although the process for making the litter is still in "batch" mode, the rate of production has significantly increased. This production rate is important for being able to provide materials for internal testing, as well as external evaluation of materials for clumping and odor control.

The scale-up process has so far been extremely useful with regard to learning how to make these materials efficiently. Materials of construction issues have arisen, and have been corrected. Additionally, we have determined the appropriate flow rate of the binder system used for agglomeration. We are currently getting about a 70% yield of useable product for litter materials (based on the sieve size), and the product appears strong and very water absorbent.

During subsequent quarters, we were able to manufacture 1000 lbs of litter for testing. 600 pounds of non-clumping animal litter and 400 lbs of clumping litter were made for various testing. Several types of fly ash were used from two different coal fired power plants to make these materials. The differences between the types of ash used were minimal. Producing 1000 lbs of animal litter required several pieces of process equipment to be purchased and installed. The manufacturing process was dramatically improved over the course of this development work. For instance, a drying step was introduced to lower the residual moisture level in the pelletized material from ~8wt% to less than 2wt%. A large drying oven was purchased and installed. There were several other process improvements that were introduced as well. The final step of the process was packaging. We packaged our material into 10 lb bags of litter for our testing purposes. These litter bags will be shipped to our own labs to quantify the settling amount. We will also perform humidity testing on these materials, to determine if they are as effective in more humid areas of the country. Additional clumping and odor control testing will also be done on the materials.

Task G: Reporting

1. **Planned Activities:** The Yearly report for FY 10 was planned and completed according to the Federal requirements. It has been uploaded to the PMC.

Patents: 1. US Patent Filed September 15, 2010 entitled "Environmentally Friendly Animal Litter". Inventors: Chett J. Boxley and Jessica McKelvie.

Publications / Presentations: None.