

Trace-Metal Scavenging from Biomass Syngas with Novel High-Temperature Sorbents

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EXECUTIVE SUMMARY

Effective syngas cleanup is one of the remaining major technical challenges yet to be resolved and one that will provide the most benefit to the suite of bio-thermochemical process technologies. Beyond tars and acid gases, which are themselves a significant detriment to reforming catalysts and associated equipment, semi-volatile metals can also damage cleanup systems, catalysts, and contaminate the fungible products. Metals are a difficult challenge to deal with whether using hot-gas filtration or low-temperature processing. Even though most of the metal tends to condense before the barrier filter of hot-gas cleanup systems, some small percentage of the metal (large enough to damage syngas-reforming catalysts, the candle filters themselves, and gas turbine blades) does pass through these barrier filters along with the clean syngas. Low-temperature processing requires expensive measures to remove metals from the process stream. Significant costs are required to remove these metals and if they are not removed before contacting the catalyst, they will significantly reduce the life of the catalyst.

One approach to solving the metals problem is to use high-temperature sorbents to capture all of the semi-volatile metals upstream of the barrier filter, which would prevent even small amounts of metal from passing through the filter with the clean syngas. High Temperature sorbents have already been developed that have been shown to be effective at capturing semi-volatile metals from vitiated combustion effluent, i.e., high-temperature flue gas. The objective on this project was to evaluate these same sorbents for their ability to scavenge metals from inert, reducing, and real syngas environments. Subsequently, it was the objective of this project to develop designer sorbents and an injection technology that would optimize the effectiveness of these sorbents at capturing metals from syngas, protecting the barrier filters from damage, and protecting the catalysts and other downstream equipment from damage. Finally, the high-temperature sorbent technology would be expanded to look at the role that these sorbents play in relation to tars and acid gases, which are the other significant pollutants within syngas. In addition to the technology development work described above, all of the information obtained in this work was to be incorporated into a syngas speciation model, which would allow direct prediction of transformations that occur in syngas as it passes from the gasifier and the sorbent-injection section and through the barrier filters.

Unfortunately, Congressional budget cuts prevented most of this work from being accomplished. Hopefully, additional funds will be provided to this work in the future, which will allow its completion. However, at the halting point of this project, the following has been accomplished.

A major initial objective of the project was accomplished, which was to determine whether or not high-temperature sorbents found to work within vitiated air might also work in an inert environment. Kaolinite, one of the sorbents previously investigated as a high-temperature sorbent for incinerators, was found to effectively capture potassium. In addition, while previous work on short-time (i.e., 1 to 2 seconds) dispersed-phase reactions found that sorbent utilization was limited to two metal oxide species captured for every one aluminosilicate crystal structure, the present investigation found that many times higher insoluble metal/sorbent capture ratios were obtained. This result not only suggests that small additions of sorbent might be highly effective, but the fact that the products were insoluble (in part due to the temperature of sorbent

injection, i.e., < 1500 °F) may be an indication that the products are unlikely to react with, corrode, or otherwise damage the candle-filter elements. There has been little work on the capture of potassium metal vapor by high-temperature sorbents, prior to this work. The fact that potassium can be effectively captured by kaolinite clay powder is a significant finding of this work, which applies both to combustion and gasification.

There is much left to be done in this area, which if performed will greatly benefit the advancement of this technology and the world through its application.

The effect of different temperatures and pressures on the effectiveness of sorbent at capturing metal and protecting the filters needs to be evaluated.

The impact of tars on sorbents and sorbents on tars also needs to be considered, and is one of the major questions about this technology.

In order to properly investigate the parameters listed above and evaluate the effectiveness of the technology, additional measurements will need to be made, many of them quite difficult. It will be important to find a method of measuring the trace amount of metal vapor that escapes through the candle filter, during each test condition, which metal concentrations may only be in the parts per trillion range. Nevertheless, these trace emissions can damage the blades of a gas turbine and hinder the processing of the syngas into liquid chemicals and fuels, by damaging reforming catalysts or otherwise.

Finally, after the bench-scale and slipstream testing is complete, it will be necessary to have a larger-scale demonstration of this technology, to determine the full-scale type impacts this technology will have.

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INTRODUCTION

The purpose of this project was to extensively investigate *high-temperature powder sorbents* for scavenging alkali and heavy metals from biomass-generated syngas.

A major issue in many gasification systems is the inability to completely scavenge or condense trace metals, such as alkalis, and heavy metals such as lead and cadmium. Work by Southern Research Institute scientists have shown that certain aluminosilicate sorbents are effective at scavenging these metal contaminants at very high rates from combustion gases, at temperatures above 1000 °C. These same sorbents were investigated for their potential to clean biomass-generated syngas of metal contaminants, prior to the particulate collection device.

The objective of this project was to develop the technology, based on inexpensive *high-temperature sorbents* and novel applications, to condition hot syngas from biomass, while preventing the condensation of trace metals. The trace metals were expected to be reactively captured and ultimately sequestered in a benign form. Application of this technology to full-scale biomass gasifiers will allow Integrated Gasification Combined Cycle (IGCC) systems to operate with relatively high particulate-control device (PCD) temperatures, in order to obtain high cycle efficiency, without fear of damaging the gas-turbine blades with metals that have escaped the PCD. Furthermore, this technology will allow the inexpensive production of very clean syngas streams from biomass gasification for subsequent reforming into high-value products, and the *high-temperature sorbents* developed in this work will eliminate toxic metals (e.g., Pb, Cd, As, Se, and Ni) that are poised for regulation.

The reactive capture of toxic and other trace metals (i.e., Na and K) by *high-temperature sorbents* is a relatively new technology. While the mechanisms for reactive capture of Pb, Cd, and Na from single- and multi-metal systems have been greatly elucidated for temperatures above 1000 °C, including detailed quantitative kinetics and rate constants, most of the previous work has been directed toward incineration applications [1-20]. The models developed earlier [1-3, 21] to describe the heterogeneous capture mechanisms within incinerator effluent also apply to syngas applications, insofar as the conditions overlap. However, the impact of higher pressures, a larger range of temperatures, reducing environments and interactions with syngas and biomass-tar need to be elucidated. In addition, application strategies for injecting and retrieving the spent sorbents should be investigated, particularly paying attention to the impact of sorbent injection on barrier filters.

As shown in previous work [1-20], eutectic melts formed during the capture of trace metals can yield complete melting of sorbent and/or flyash particles, which could potentially stick to and plug barrier filters. This potential problem can be reasonably addressed through an understanding of the behavior of these eutectics as a function of temperature, pressure, sorbent concentration, and sorbent, flyash, and metals composition. Therefore, a detailed understanding of the relationships between trace metals and negative eutectic-melting impacts on barrier filters is needed, and the ability of these *high-temperature sorbents* to mitigate these negative impacts should also be assessed.

Previous work performed by Gale et. al. [1-4] found that inexpensive clay sorbents were capable of rapidly scavenging multiple-metal species from post-flame gases, and that high sorbent utilizations were possible. Figure 1 shows that the sorbent utilization limit for kaolinite in bimetal systems of lead/cadmium and lead/sodium was very high, even though the data in Fig. 1 [2] was taken from experiments performed in post-flame gases between 1000 °C and 1300 °C. In fact, for low equivalence ratios, the sorbent utilization limit was approximately twice that of the single-oxide (i.e., PbO, CdO, Na₂O) aluminosilicate (Al₂O₃.2SiO₂) limit for all single-metals and bi-metal systems investigated [2].

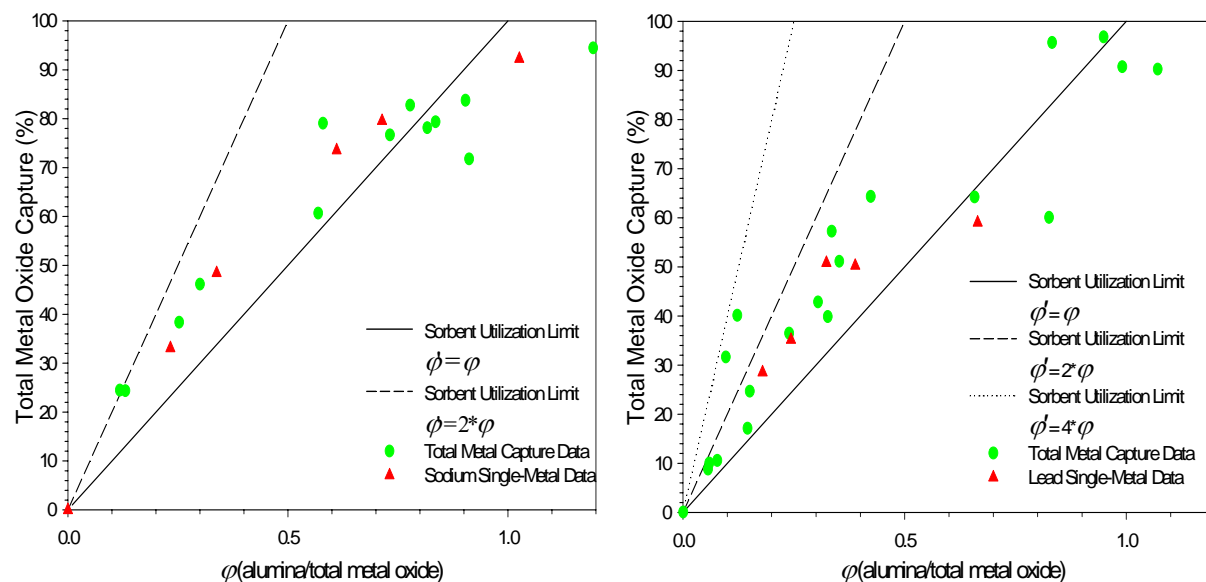


Figure 1. Metal capture by kaolinite exceeded single-oxide limit lines (Temp = 1000 to 1300°C).

Integrated gasification combined cycle (IGCC) systems require ultra-clean syngas to feed into the gas turbine, to avoid deposition and corrosion on the turbine blades. IGCC systems increase in thermodynamic cycle efficiency (generate more electricity per fuel used) the higher the gas cleanup temperature. These higher temperatures make it more likely that some small fraction of trace metal, particularly sodium, may pass through the PCD and impact the gas turbine. Furthermore, a highly-clean syngas (no metals of any kind) is required for subsequent syngas reforming to produce fuels and other high-value products.

High-temperature sorbents technology can help resolve both of these problems, effectively and inexpensively. The *high-temperature sorbents* are effective at very high temperatures (>1000 °C) [1-20], as shown in Fig. 1. In addition, the reaction products formed from the scavenging of metal by sorbents are completely removed by the PCD, because the super-micron-size sorbent particles are too large to penetrate a barrier filter. Hence, *high-temperature metal-scavenging sorbents* will alleviate the need to quench the syngas in order to remove trace metals before reforming the syngas.

Figure 2a and b contain SEMs of cadmium/kaolinite product particles sampled following sorbent injection into hot post-flame gases at 1160 °C and 1280 °C respectively [3]. At the lower temperature condition, the captured cadmium did not cause the sorbent particle to melt (see Fig. 2a), while the slightly higher temperature (~120 °C) caused complete melting and sphere

formation (see Fig. 2b). For the reaction of lead and sodium with kaolinite however, a eutectic melt occurs at much lower temperatures, and spherical particles are observed following sorbent injection at the *low and high* temperatures [1]. This melting, which is caused by the eutectic formed between the metal/sorbent reaction product and the remaining *unreacted* sorbent, plays multiple significant roles in the metal-capture process [1-5].

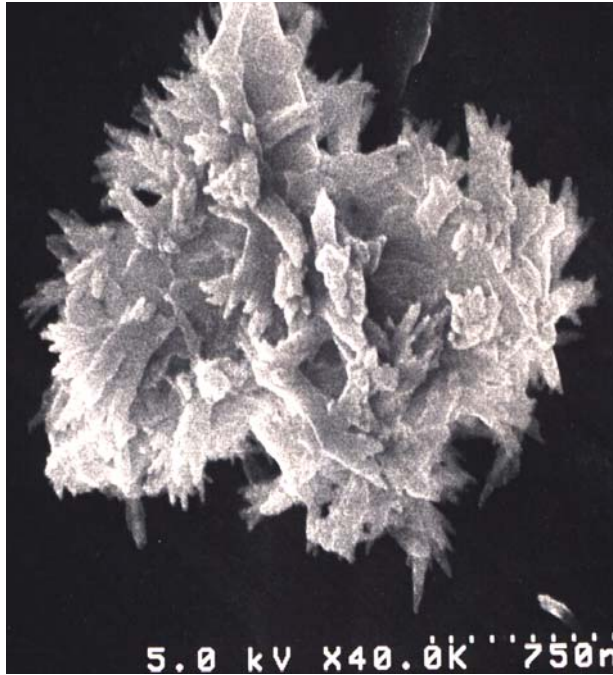


Figure 2a. Sorbent injection at 1160 °C.



Figure 2b. Sorbent injection at 1280 °C.

The fundamental processes of semi-volatile metal reaction with kaolinite in high-temperature entrained-flow environments [1, 2] are summarized as follows: Soon after injection, kaolinite flash-calcines to form layers of single meta-kaolinite (aluminosilicate) crystal platelets separated by open meso-pore gaps. Hence, transport limitations are minimal and most of the active sites are on available surface. At relatively low temperatures, the reaction rate is slow, limited by the closely packed crystal structure and aluminosilicate reaction rate. At higher temperatures, the initial products are aluminosilicates, but these initial products induce a eutectic-melt that breaks down the closely packed crystal structure, thus allowing more degrees of freedom and greater capture. As the reaction continues, the aluminosilicate structure breaks down completely, allowing the formation of silicates and aluminates. In the case of sodium, silicate and aluminate products allow for at least twice the sorbent utilization available for sodium-aluminosilicate reaction products alone [2, 5]. At still higher temperatures, the eutectic-melt becomes excessive, thus filling-in the meso-pore gaps lying between the platelets, and the sorbent is deactivated before complete sorbent utilization can be achieved [1-5].

Previous research [3, 5] has shown that cadmium forms a much higher temperature eutectic than does lead or sodium. In fact at 1160 °C, the eutectics formed by lead and sodium already initiate excessive partially-deactivating melts [1, 2, 5], while cadmium does not even initiate a melt sufficient to induce enhancement [3, 5]. However, cadmium does initiate melting (see Fig. 2b) and very significant capture-enhancement at 1280 °C [1, 3, 5-6]. The cadmium eutectic initiates

excessive melting and sorbent deactivation at a higher, yet to be determined, temperature (i.e., >1300 °C).

Eutectic melting also plays a significant role in multi-metal systems, as the major parameter controlling multi-metal enhancement and inhibition mechanisms. The extent of metal/kaolinite particle sphericity was quantified as a function of particle metal species concentration for a given temperature condition (max temp. = 1160 °C), using energy dispersive spectroscopy (EDS). Spherical and oblate particles experienced the most melting and restructuring, while the crystalline particles experienced little. Figure 3 shows the influence of cadmium on melt-associated kaolinite particle transformations versus the combined influence of lead and sodium. As shown, the presence of cadmium at 1160 °C caused little kaolinite structural transformation and sphere formation, whereas the presence of lead or sodium at this temperature significantly increased such transformations. This enhancing-melt initiated by the lead and sodium products, in the presence of cadmium, significantly enhances cadmium capture by kaolinite [1, 5]. In addition, Fig. 3 indicates that the presence of cadmium in a particle tends to inhibit the melting caused by lead and sodium at that temperature, and by this means cadmium may enhance lead and sodium capture, by reducing excessive-melt induced deactivation, as published [1]. Metal-scavenging models have been developed [1-3] that include each of these eutectically-induced melt-driven enhancement and inhibition mechanisms.

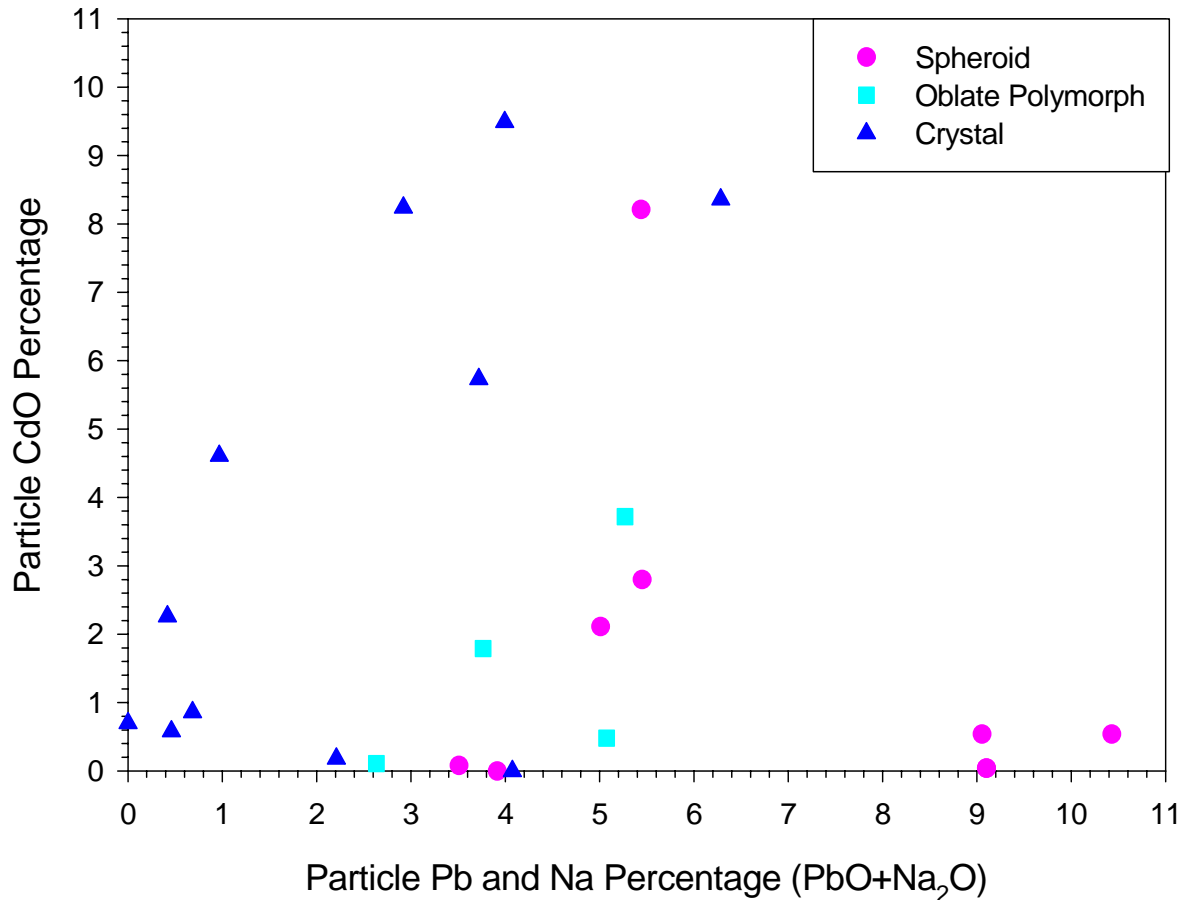


Figure 3. Effect of Cd versus (Pb + Na) on melting of dispersed kaolinite particles at >1000 °C.

Multi-metal interactions with kaolinite are complex. Cadmium capture on kaolinite is enhanced by the melting and restructuring of the meta-kaolinite crystal caused by the presence of lead and/or sodium, at temperatures between 1000 °C and 1300 °C [1]. Cadmium in turn enhances the capture of lead and sodium by preventing sorbent deactivation [1]. Hence, total metal capture is significantly enhanced for the bimetal system of lead and cadmium in the temperature range 1000 °C to 1300 °C, due to the formation of an optimum eutectic-melt [1, 5]. For the same temperature range, competition between sodium and lead capture on kaolinite, strongly favors sodium capture [1]. A higher reaction rate allows sodium to dominate through direct competition and also by reacting with the sorbent before the deactivating-melt, initiated by sodium or lead products, significantly deactivates the sorbent [1]. Sodium also dominates by effectively displacing lead already captured, possibly by causing lead aluminosilicate products to break down into lower order sodium and lead silicates and aluminates [1].

A detailed understanding of eutectic melting relationships with metal scavenging, as discussed above and illustrated in Figs. 2 & 3, is also essential to developing harmonious particulate collection strategies with benign effects on barrier filters. While it is true that a modicum of melting might be desirable for optimum metal scavenging, excessive eutectic melting of sorbents or flyash can cause severe problems for PCDs. Even if the particles that collect on a candle filter are not molten when they are collected, it is possible in some cases for the dust cake collected on the filter to continue to react with metal and melt while resting on the filter surface. Eutectic melting of the dust layer on candle filters could make the dust cake difficult to remove, may clog the filter, and may cause bridging between candles, all of which are highly undesirable. However, a detailed understanding of the governing kinetics and the eutectic formed as a function of the syngas environment and sorbents injected will allow design of sorbent scavenging technologies that prevent damage to the PCD and optimize the sorbent technology along with the PCD operating conditions to obtain the most effective metal-scavenging technology available.

Figure 4 shows the soluble and insoluble products of reactive sodium capture by kaolinite powder sorbent particles entrained in post-flame gases for less than 1 second above 1000 °C. As shown, the sorbent was effective at removing the sodium from the hot gas. Sorbent utilizations were very high (i.e., two Na₂O structures were formed within the sorbent particles for every one Al₂O₃.2SiO₂ structure, at the low equivalence ratios), [2]. Figure 4 also shows the relative amounts of soluble and insoluble products. The obtaining of these data was possible because of the advanced Aerosol Size Fractionation Method (ASFM) used to determine the extent of reactive metal capture by sorbents and sorbent utilization, independent of product or sorbent solubility [5]. This added information on *reactive-product* solubility, along with information from the phase diagram of metal/sorbent systems (i.e., sodium and lead aluminosilicates), enabled the determination of the products formed (i.e., silicates, aluminates, and aluminosilicates) and an explanation of the governing single- and multi-metal enhancing mechanisms [1-5].

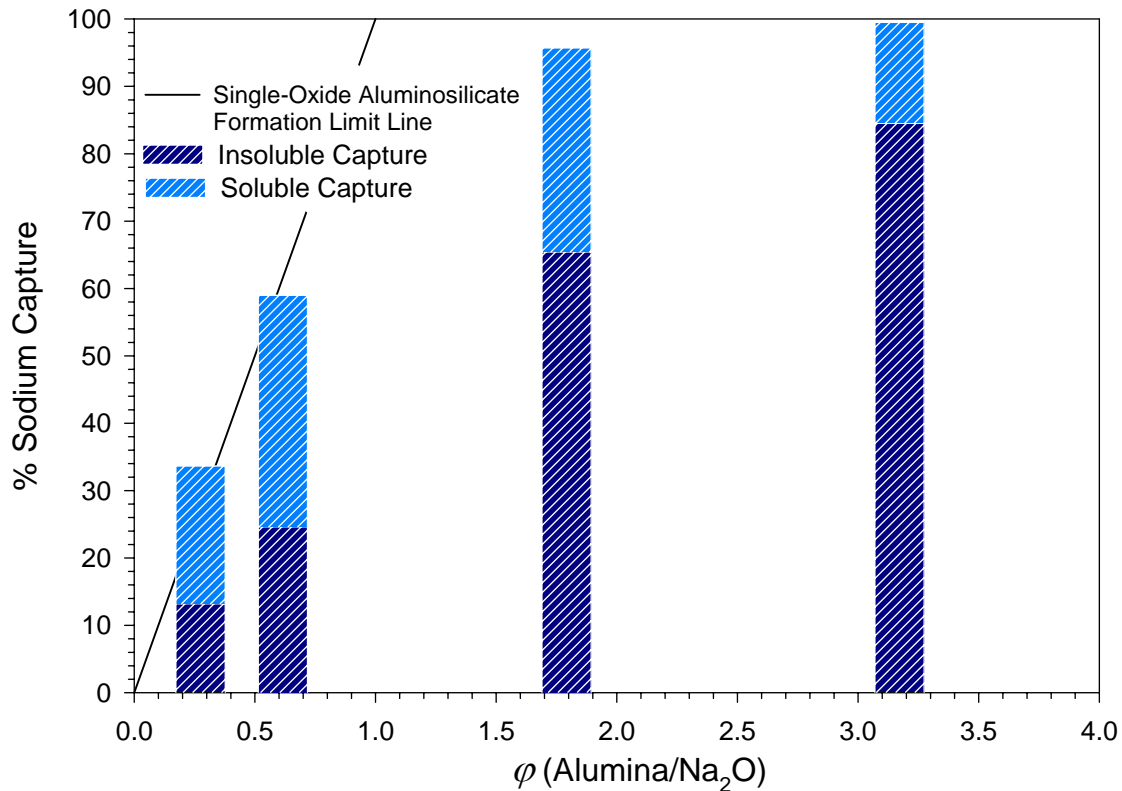


Figure 4. Soluble and insoluble products of sodium reactively captured by kaolinite [2].

This project was intended to extensively investigate high-temperature powder sorbents for scavenging trace alkali and heavy metals from coal-generated syngas. Unfortunately, budget cuts from Congress have severely limited this work.

A major issue in many gasification systems is the inability to completely scavenge or condense trace metals, such as alkalis, and heavy metals such as lead and cadmium. As discussed above, work by Southern Research Institute scientists [1-20] has shown that certain aluminosilicate sorbents are effective at scavenging these metal contaminants at very high rates from combustion gases, at temperatures above 1000 °C. These same sorbents will be investigated for their potential to clean syngas of metal contaminants, prior to the particulate collection device (PCD).

While the governing mechanisms for metal scavenging by high-temperature sorbents are well understood for excess-oxygen flue gas, the added complexity of gasification systems, syngas, and reducing environments have not been fully investigated. The purpose for this work was to investigate the impact of syngas environments (i.e., reducing environments, tar contamination, additional competing species for reaction, and high pressures) on the scavenging of metals by these sorbents. The resulting mechanisms were to be included in a model, currently being developed by Southern Research Institute [22] in partnership with UAB, to predict speciation within hot-gas cleanup systems for biomass gasification. Unfortunately, once again, the modeling has stopped for now, because of the budget cuts.

In addition to scavenging mechanisms, sorbent injection and collection procedures should be investigated. Among other things, the impact of reacted metal/sorbent particles on barrier filters needs to be examined, considering both the ability to collect and remove these particles and any deleterious effects on the filters.

A pilot-scale slip-stream at the Power Systems Development Facility (PSDF) is used both to provide real and simulated syngas (depending on the experiment), representative of the syngas stream produced in a full-scale biomass gasifier.

The following list of unknowns needs to be elucidated:

- 1) Scavenging rate constants for K, As, Se, Cd, Pb, and Na (rate constants have already been obtained at atmospheric pressure for the capture of Pb, Cd, As, and Na by several sorbents).
- 2) The effect of pressure on the capture rate of all metals, and the effect of pressure on multi-metal interactions, melting enhancement, and melting inhibition.
- 3) The effect of tar and syngas (reducing environment) on metal capture by sorbents. Reducing environments will likely change the reactive form of metal vapor in the syngas. In combustion environments, the metal vapors typically exist as oxides, hydroxides, chlorides, or form sulfur compounds. Oxides are much less prevalent in syngas, with a greater potential for some elemental metal forms.
- 4) Sorbent utilization, and a quantitative relationship between metal capture and sorbent composition.
- 5) Detailed mechanisms describing the metal scavenging process in hot-gas cleanup.
- 6) Sorbent collection issues and effect of sorbents on barrier filters.

The extent to which the unknowns listed above are elucidated in the investigation depends on the complexity of interactions as yet undiscovered. However, it is anticipated that between 300 and 500 different conditions should be investigated in parametric investigations. All of the mechanisms elucidated and information gained from the parametric tests will be incorporated into a hot-gas cleanup model currently being developed by SRI and UAB [22].

EXPERIMENTAL

Nomenclature for the Experimental Section

$C_{m,s}$	concentration of metal salt vapor adjacent to the liquid surface, kmol/m ³
$C_{m,\infty}$	concentration of metal salt vapor in the free stream, kmol/m ³
d	jet nozzle diameter, m
$d_{p,1}$	size of char particles, m
$d_{p,2}$	size of sorbent particles, m
D	molecular diffusion coefficient of NaOH or KOH, m ² /s
E	joint efficiency, dimensionless, = 1 for seamless tube
i.d.	inside diameter, in., m
k	Boltzmann constant, = 1.38×10^{-23} J/K
N_1	number density of char, m ⁻³
N_2	number density of sorbent, m ⁻³
o.d.	outside diameter, in., m
p_t	rated working pressure, psi
P	internal design pressure, psi
PSDF	Southern Company/DOE Power Systems Development Facility
R	inside radius, in., = 0.69 in.
S	reactor inside diameter, m; maximum allowable stress value, psi, = 500 psi at 1800°F (Code Case 1983, ASME, 1985)
Sh	Sherwood number, dimensionless
t	thickness of shell, in., = 0.140 in.
T	temperature, °F, K
\dot{V}	volumetric flow rate of nitrogen, at temperature, m ³ /s
μ	gas viscosity, kg/(m·s)

Reactor Design

The Hot-Gas Cleanup Slipstream Reactor (HGCSR) was designed for examining syngas-cleanup technologies. The reactor is made of H800 alloy and is very suited for the 900 °C condition to be tested. A diagram of the flow system is shown in Figure 5.

High Temperature Sorbents Project
 Flow Diagram for Experiments Using Mini-Reactor
 Version 9, August 7, 2006

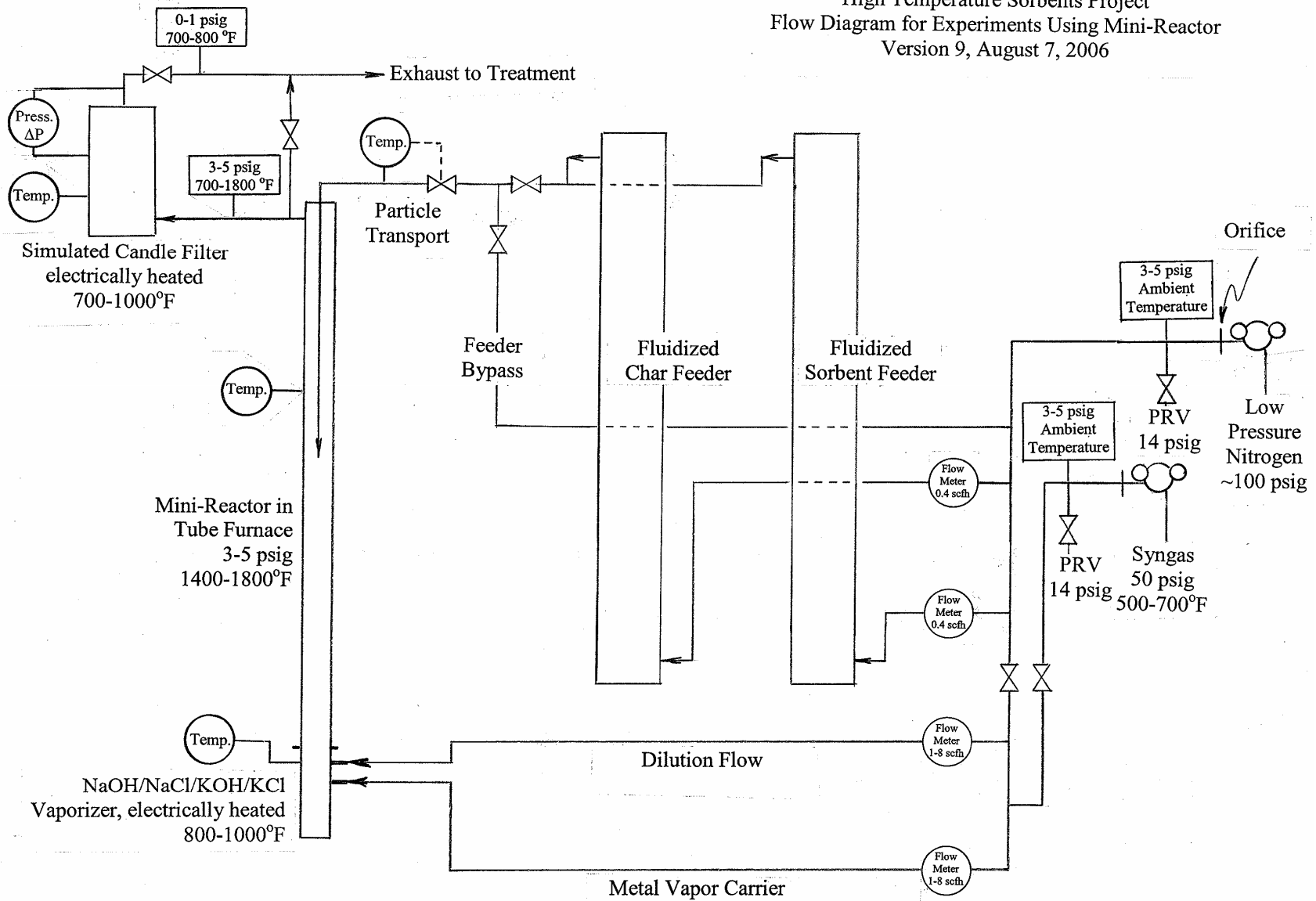


Figure 5. Flow diagram of the system for investigation of trace metal scavenging by high temperature sorbents.

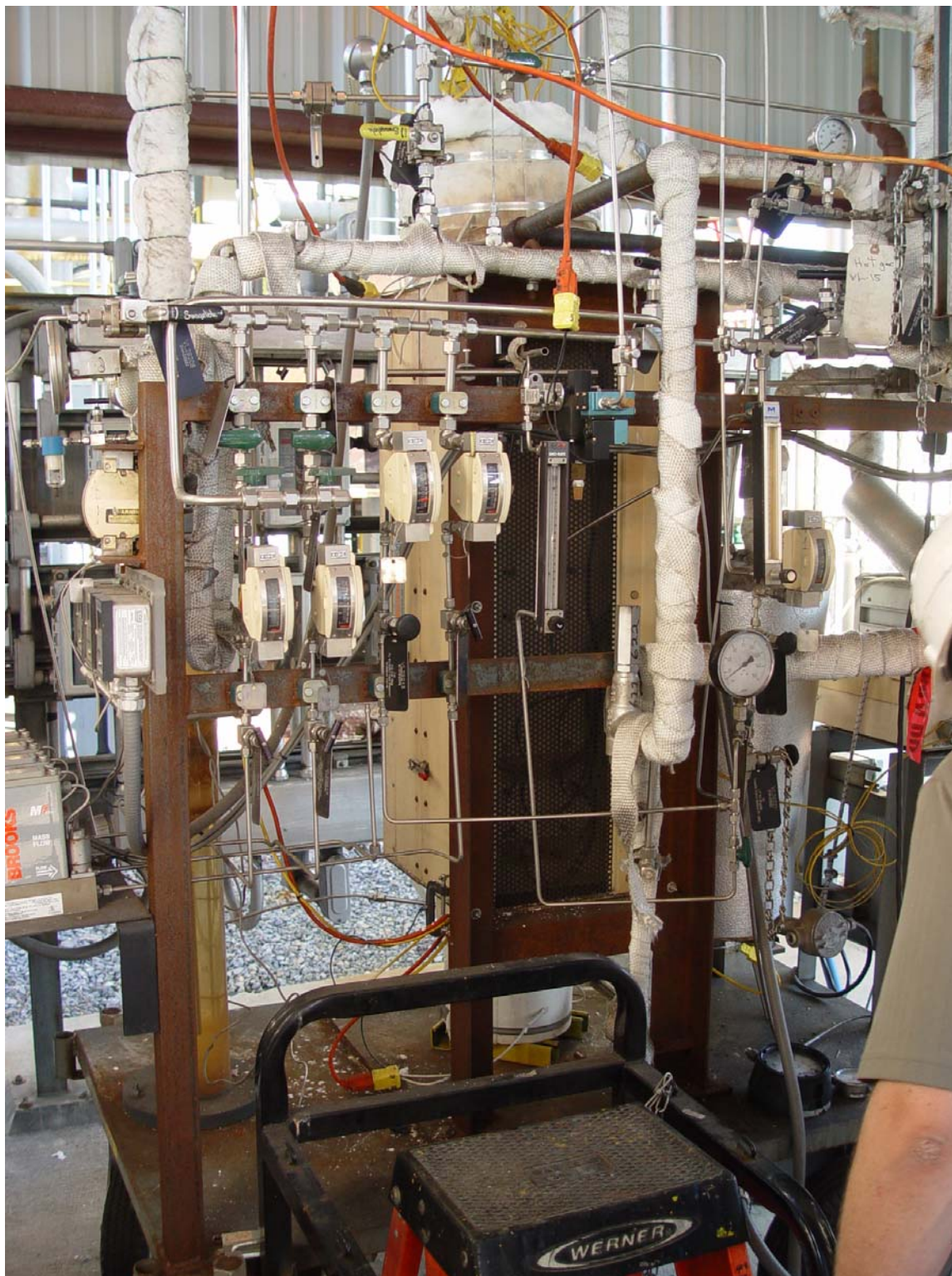
The bottom and center sections of the reactor are made out of H800 alloy, capable of withstanding high temperatures and resisting corrosive components commonly found in syngas. The top section is made of stainless steel, and is maintained at relatively low temperatures. The central section of the reactor is approximately 44 inches long. The inside diameter of the reactor is about 1 ½ inches. The tubes entering the bottom of the reactor allow for the feed of nitrogen or syngas. One of the two tubes entering the reactor points down into the lower section of the reactor, for the purpose of vaporizing metals inside the reactor. The top of the reactor houses a small candle filter, through which the syngas must pass, preventing any particulates from escaping. This reactor was designed for use at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama, a U.S. Dept. of Energy/Southern Company gasification-demonstration research facility. However, a heater, flow meters, and other apparatus have been assembled at Southern Research Institute in Birmingham, to allow offsite testing with this reactor, using simulated syngas, including spiked metals.

The nitrogen and syngas are regulated at pressures between 3 and 5 psig. The flow is divided into four streams: (1) 0.4 scfh of nitrogen to the fluidized sorbent particle feeder, (2) 0.4 scfh of nitrogen to the fluidized char particle feeder, (3) 1 to 8 scfh of nitrogen or syngas to the metal vaporizer, and (4) 1 to 8 scfh of nitrogen or syngas to the base of the reactor to dilute the metal vapor to the desired level, in the range from 10 to 1000 ppmv and achieve the desired total flow rate into the reactor, ~ 10 scfh. The vaporizer is held at a temperature in the range from 600 to 1000 °F, depending on the metal concentration desired. The diluted metal vapor travels upward through the reactor at approximately 1 ft/s. The temperature in the central heated zone is between 1400 °F and 1800 °F. The flow of entrained sorbent from the fluidized-bed feeder is introduced through a tube running down the center of the reactor, starting at the top of the reactor and ending at a point that provides the desired residence time of sorbent in contact with metal vapor, typically 1 to 2 seconds.

At the exit of the reactor, the gas and suspended particles are cooled to a temperature representative of the particulate control device in a full-scale gasifier hot-gas cleanup system. The current candle-filter temperature for the PSDF hot-syngas cleanup system is typically 800 °F. The filter medium, pore size, and face velocity are also representative of full-scale equipment. When the filter cake has built up to a thickness (pressure drop) at which it would be back-pulsed in full-scale operation, the system is cooled down and the filter disassembled for determination of the chemical and physical properties of the dust cake. Of particular interest are the efficiency of metal capture, interactions among sorbent particles (e.g. sintering), and interaction between particles, metal vapor, and the filter.

The Pall Corporation, supplier of iron aluminide filter elements for the particulate control device at the PSDF, fabricated short filter elements for the present experiments using the same iron aluminide filter medium and diameter as used at full scale. A drawing of the filter element is attached as Appendix A. A new filter was installed for each run.

A photograph of the equipment in place in the Mini-Reactor test facility at the PSDF is shown in Figure 6.



Photograph by K. Paul Conner, Southern Company

Figure 6. Photo of the reactor furnace and flow system for investigation of trace metal scavenging by high temperature sorbents.

A photograph of the reactor assembly, consisting of the metal salt vaporizer, reactor tube, and filter housing, is shown in Figure 7. Based upon their experience, engineers at the PSDF recommended INCOLOY alloy 800H (UNS N08810) as the material for the main section of the reactor. The reactor was fabricated using INCOLOY alloy 800H Schedule 40 seamless pipe, (1.66 in. o.d. and 0.140 in. wall thickness). The ASTM Specification Number on the pipe is SB-407. Properties of the material are specified in a document available from the Special Metals Corporation [23].

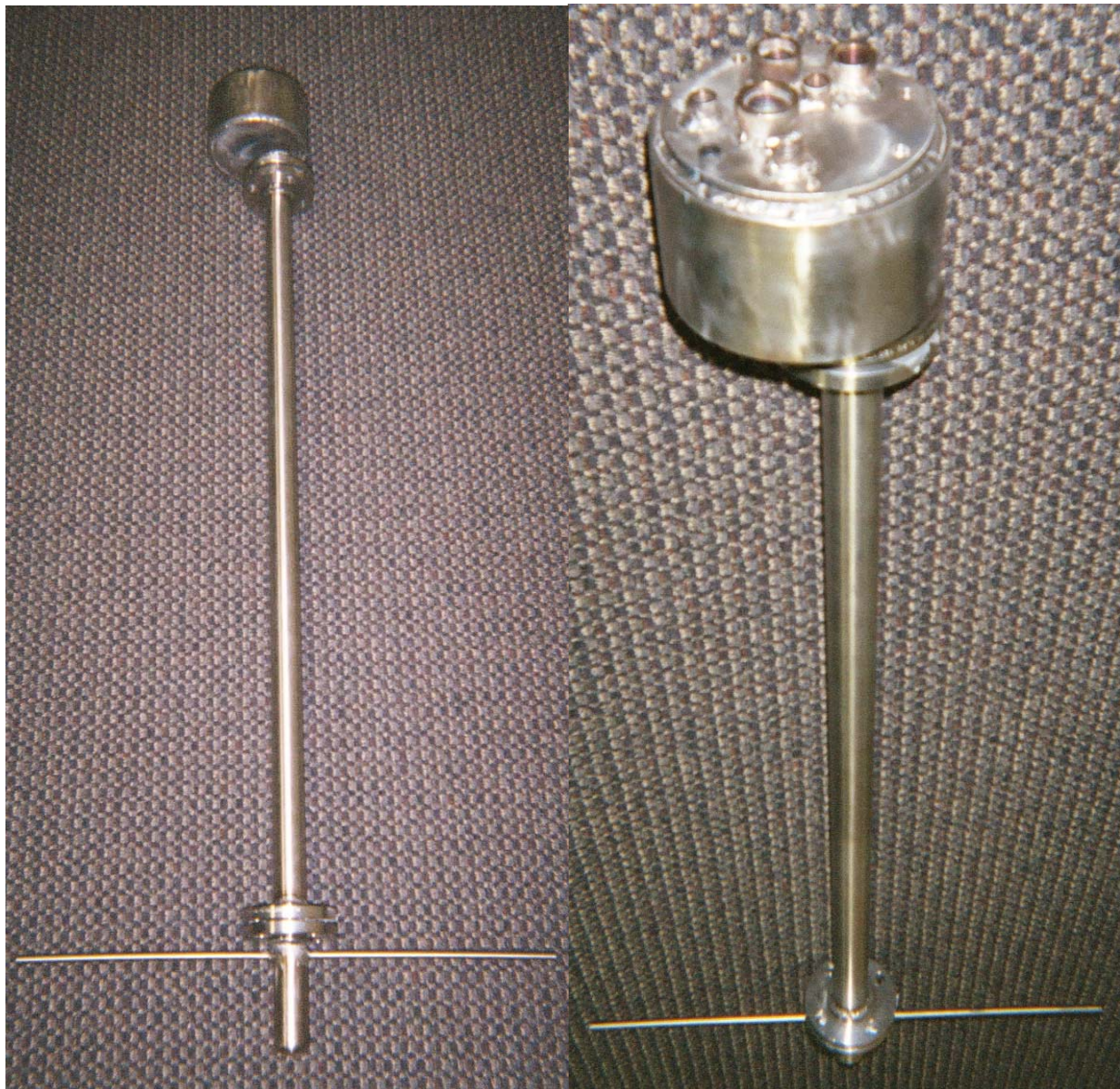


Figure 7. Reactor assembly – metal salt vaporizer (bottom), reactor tube (center), and filter housing (top).

INCOLOY alloy 800H is approved under the Boiler and Pressure Vessel Code of the American Society of Mechanical Engineers [24]. Rules for construction of pressure vessels are defined

under Section VIII, Divisions 1 and 2. Design stress values for alloy 800H for Section VIII, Division 1 construction are listed in Table 1B of Section II (Materials), Part D (Properties) and also addressed by Code Case 1983 [25], for service up to 1800 °F.

The allowable working pressure of the Mini-Reactor pipe is given by ASME, 2001, Section VIII, Division 1, Part UG-27, [24] - p. 23:

$$P = \frac{SEt}{R + 0.6t} \quad (1)$$

The symbols and values of the parameters are as follows:

E	joint efficiency, dimensionless, = 1 for the seamless tube
P	internal design pressure, psi
R	inside radius, in., = 1.38 in.
S	maximum allowable stress value, psi, = 500 psi at 1800 °F (Code Case 1983, ASME, 1985)
t	thickness of shell, in., = 0.140 in.

Substituting the values in Equation (1):

$$P = \frac{(500)(1)(0.140)}{(1.38) + (0.6)(0.140)} = 47.8 \text{ psi} \quad (2)$$

The flanges on the main reactor tube are Class 150, also fabricated from INCOLOY alloy 800H. The ASTM Specification Number on the flanges is SB-408.

Pressure-temperature ratings for INCOLOY alloy 800H flanges are specified in U.S. customary units in Table F2-3.15 of *Pipe Flanges and Flanged Fittings* (ASME, 2004 [23], p. 154). The method for calculating the pressure-temperature ratings is specified in Annex B. For Class 150 flanges (ASME, 2004 [26], p. 104):

$$p_t \leq 320 - 0.3 T \quad (3)$$

The symbols are as follows:

p_t	rated working pressure, psi
T	material temperature, °F

The material temperature, T, is not to exceed 1000 °F. Substituting this value in Equation (3):

$$p_t \leq 320 - (0.3)(1000) = 20 \text{ psi} \quad (4)$$

The maximum temperature and corresponding maximum rated working pressure for the flanges are therefore: *Maximum temperature:* 1000 °F *Maximum rated working pressure:* 20 psi

Metal Salt Vaporizer

The metal salt vaporizer, shown at the bottom of Figure 7, is intended to deliver metal salt vapor at a rate and concentration that can be adjusted by variation of the temperature and dilution gas flow rate. Molten salt sits at the bottom of the reactor, where the inside diameter is 35 mm (1.38 in.). A single tube carrying nitrogen or syngas is directed downward, normal to the liquid surface. The gas jet issuing from this tube impinges on the surface and forms a "wall jet" that spreads out radially over the surface. At the reactor wall the flow turns upward, against the incoming nitrogen jet, and is diluted with another stream of nitrogen or syngas as it moves into the main part of the reactor.

Mass transfer between the horizontal liquid surface and the vertical impinging jet is treated in several publications. Scholtz and Trass analyzed mass transfer in laminar wall jets [27] and in impinging jets having fully-developed parabolic velocity profiles at the jet nozzle, for jet Reynolds numbers in the range from 375 to 1970 [28]. Martin [29] reviewed the literature on heat and mass transfer in isolated impinging jets and arrays of jets, including both the stagnation and wall jet regions, for jets having Reynolds number greater than 2000 and uniform inlet velocity profiles. The latter work is the basis for the presentation of the topic of impinging jets by Incropera and DeWitt [30].

None of the literature cited above considers a jet surrounded by an enclosure, as in the vaporizer. However, our situation is similar to that of a jet in the midst of an array of jets, because the flows from neighboring jets in an array also turn upward when they meet each other, as if surrounded by a wall. Although the boundary conditions in these two cases are different, the details of the upflow away from the surface are not expected to have great influence on mass transfer at the surface. Martin [29] and Incropera and DeWitt [30] specify the optimum geometry for maximum mass transfer from the surface to the gas in an array of jets: (1) nozzle diameter should be $1/7^{\text{th}}$ of the spacing of the jets (the spacing is equivalent to the reactor tube diameter here), so the jet diameter should be $35/7 = 5$ mm (0.197 in.), and (2) height of the nozzle above the surface should be 5 times the nozzle diameter, or 25 mm (~1 in.).

Consider the vaporization of NaOH and KOH, whose equilibrium vapor pressures are shown as functions of temperature in Figure 8. For the present calculation, we choose a temperature of 1000 K (727 °C, 1341 °F), at the low end of the range shown, where the vapor pressures of NaOH and KOH are on the order of 150 Pa, giving an approximate mole fraction of 1500 ppm in saturated gas adjacent to the molten salt surface. The optimum dimensions specified above and the temperature determine the flow conditions. The Reynolds number for the nitrogen jet is 250, unfortunately outside the range for the arrays of jets considered by Martin [28] and Incropera and DeWitt [30]. Instead, we rely on the isolated jet analyses of Scholtz and Trass [27, 28]. A somewhat lengthy derivation, starting from the correlations for local Sherwood numbers given by Scholtz and Trass, provides a value of 3.8 for the average Sherwood number for the present configuration. The Sherwood number obtained by extrapolation of the correlation by Martin [29] for an array of jets, valid only for Reynolds numbers greater than 2000, is 3.3.

The following equation was solved for the NaOH or KOH concentrations in the free stream, after passing over the molten salt surface (please see the Nomenclature Section for definitions of the symbols):

$$C_{m,\infty} = \frac{1}{\dot{V}} \frac{Sh D}{d} \frac{\pi S^2}{4} (C_{m,s} - C_{m,\infty})$$

Taking a flow rate of nitrogen in the middle of the design range, 1.2×10^{-4} actual m^3/s (4.5 scfh), 700 mol ppm of metal salt vapor are expected in the gas leaving the vaporizer. The mole fraction can be adjusted using the dilution flow, in combination with adjustment of the nitrogen flow to the jet, in addition to variation of the temperature. Having chosen a low temperature for the present estimate provides a wide margin for adjustment of the metal salt vapor pressure, should the Sherwood number for the enclosed jet be lower than the estimate based upon the analysis for an isolated jet. In fact, the vaporizer delivered much more metal salt vapor than expected, as described later in the section on the experiments.

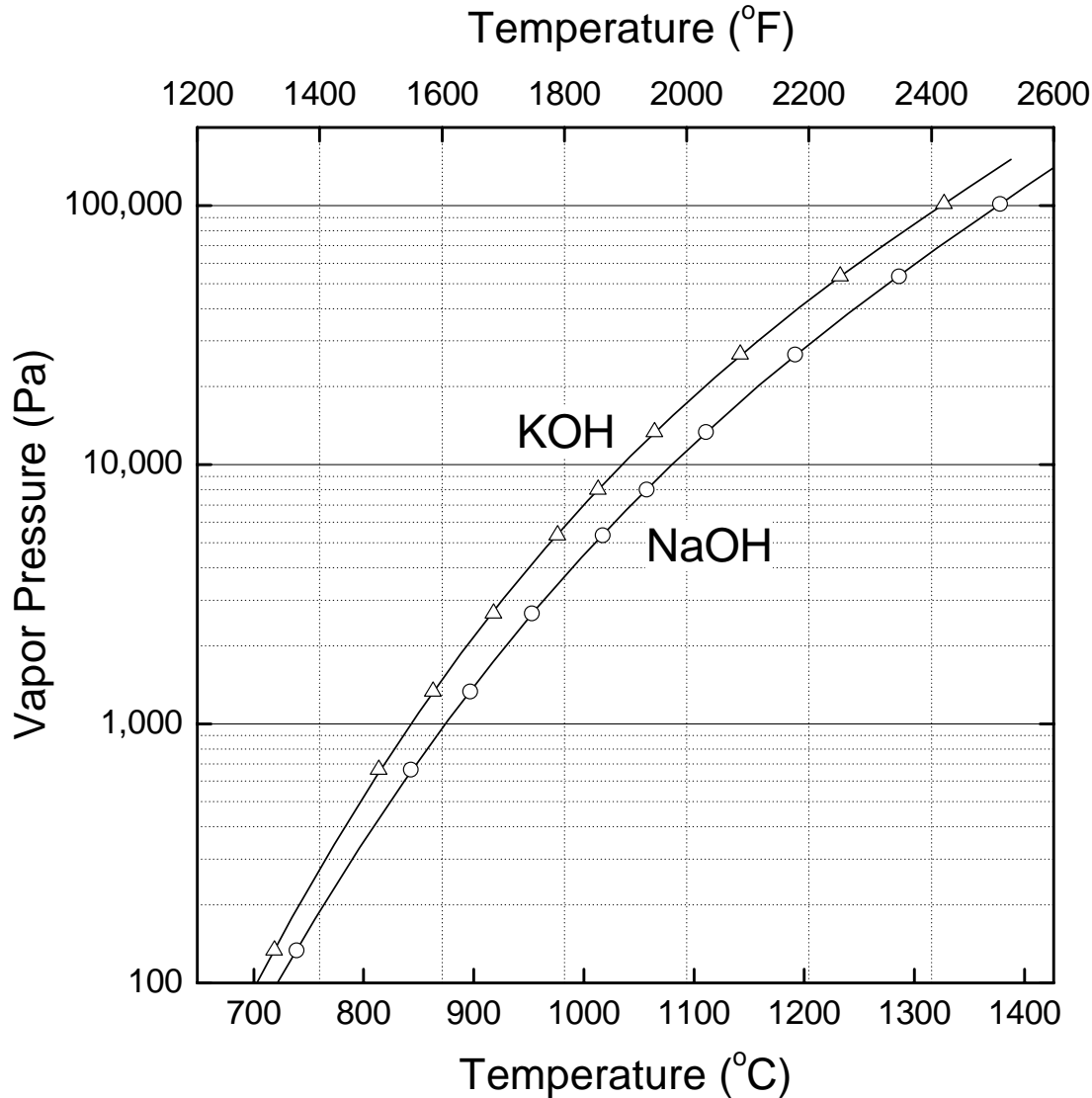


Figure 8. Equilibrium vapor pressures of NaOH and KOH as functions of temperature [31].

Sorbent Feeding

The sorbent (kaolinite clay powder) was delivered from a fluidized bed. The fluidized bed was constructed using 0.500 in. o.d., 0.035 in. wall, Type 316 stainless steel tubing. A pneumatic vibrator was clamped to its side. The kaolinite was first dried overnight in an oven at 105 °C. Four grams of dried sorbent were charged in the sorbent feeder. The development and calibration of the feeder were accomplished using a bed constructed from polystyrene tubing, so the behavior of the bed under different loadings and gas flow rates could be seen. There is a rapid decline in the delivery rate with time over the first several hours of feeding, as fine particles are elutriated from the bed. This initial period is followed by one during which the solid flow rate decreases more slowly. Because of this unwanted phenomenon, each fresh charge of kaolinite was fluidized for 3 hours to remove fine particles, before connecting the fluidized-bed feeder to the reactor. The rate of kaolinite delivery from the optimized bed design is shown as a function of time in Figure 9.

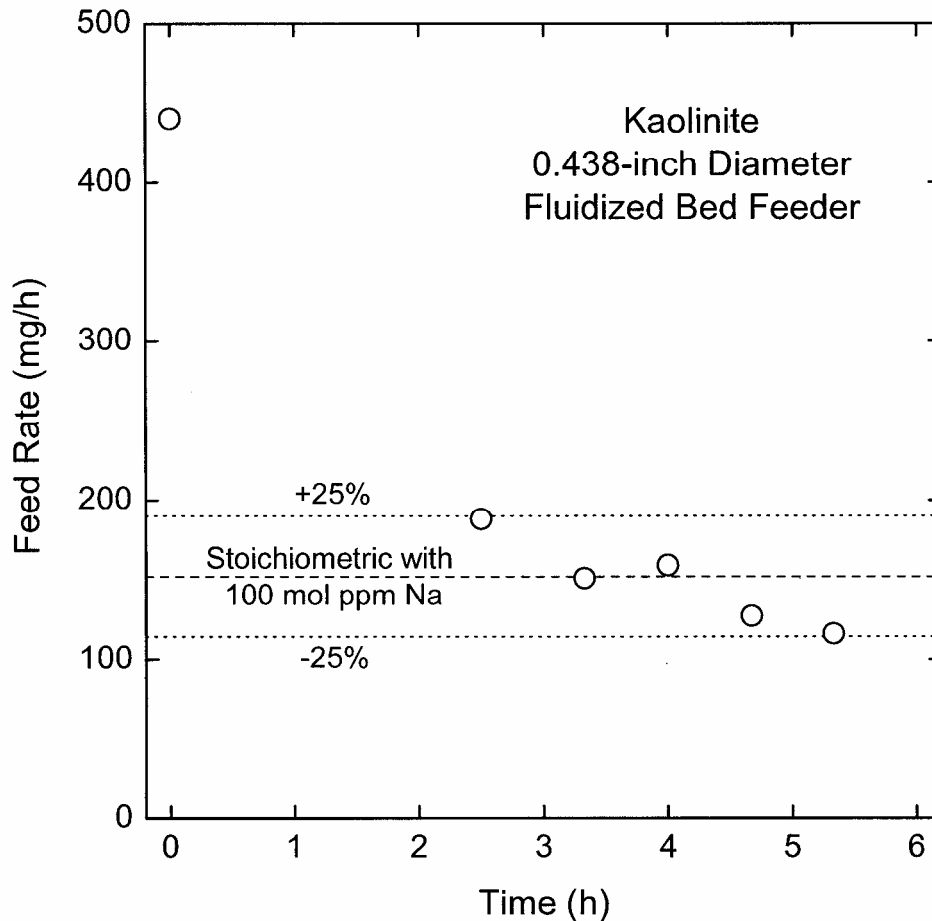


Figure 9. Calibration plot for delivery of kaolinite by the fluidized-bed sorbent feeder. The fluidized bed was constructed of polystyrene tubing, with an inside diameter of 0.438 inches.

Engineers at the PSDF did not feel that the use of the polystyrene feeder was sufficiently safe, because, in the event that the flow from the feeder to the reactor reversed during an upset condition, the plastic would be exposed to hot gas. The material was therefore changed to

stainless steel, as described above, having an inside diameter close to that of the polystyrene prototype. The feed rate from this system was somewhat less than perfectly stable and consistent. Unfortunately, commercial feeders currently available are not able to feed as low of a sorbent feed rate with as low of a carrier gas flow stream as required for these tests. Considering the situation and the challenge, the sorbent feeder has performed remarkably well.

Coagulation of Sorbent and Char Particles

Kaolinite powder was the only sorbent fed to the reactor during the experiments described in the present report. However, before the budget cut, it was planned for both sorbent and char to be fed to the reactor, to reproduce the environment that a sorbent would encounter in the actual application. Under those conditions, the question arises whether coagulation of sorbent particles with char might increase the effective size of the sorbent and inhibit mass transfer of metal vapor species from the gas to the sorbent surface. The heterogeneous coagulation rate of the two types of particles was estimated, as described below.

The rate of coagulation ($\text{m}^{-3}\text{s}^{-1}$) of particles of different size in the continuum regime is given by Seinfeld ([32], pp. 391-394):

$$\frac{\Delta N}{\Delta t} = \frac{2kT}{3\mu}(d_{p,1} + d_{p,2}) \left(\frac{1}{d_{p,1}} + \frac{1}{d_{p,2}} \right) N_1 N_2 \quad (5)$$

where N is particle number density, d_p is particle size, the subscripts 1 and 2 distinguish the two types of particles, $\Delta N/\Delta t$ is the rate of change in number density of either type of particle, k is the Boltzmann constant, T is absolute temperature, and μ is gas viscosity. The values chosen for the calculation are given in Table 1.

Table 1. Values of the Parameters Used in the Calculation of the Coagulation Rate of Sorbent and Char.

Parameter	Symbol	Value	Source
Number density of char	N_1	$8 \times 10^{10} \text{ m}^{-3}$	a
Number density of sorbent	N_2	$9 \times 10^7 \text{ m}^{-3}$	b
Size of char particles	$d_{p,1}$	16 μm	a
Size of sorbent particles	$d_{p,2}$	10 μm	typical
Temperature	T	1173 K	typical
Gas viscosity	μ	$4.6 \times 10^{-5} \text{ kg}/(\text{m}\cdot\text{s})$	nitrogen

a. Experience at the PSDF [33].

b. Burgess-40 kaolinite, 10 μm mean particle size, stoichiometric with 100 ppmv Na.

Substitution of the values in Eq. (5) gives a coagulation rate of $7000 \text{ m}^{-3}\text{s}^{-1}$, an initial rate of less than 0.01% of the total sorbent particles in the feeder per second. Even allowing for augmentation of the coagulation rate by one to two orders of magnitude due to turbulence ([32], p. 400), the rate of sorbent/char particle coagulation is still small. Inhibition of sorbent activity by this mechanism is not expected to be significant.

When both sorbent and char particles are fed into the flow reactor, they should, however, be fed from separate fluidized beds, because if the two types of particles are mixed together as powders and fluidized together, they are less likely to separate during injection and may not be representative of sorbent injected in a full-scale process.

Description of Testing

Table 2 shows the six conditions tested in the slipstream test facility. The sorbent injector was placed at the axial position in the reactor that provided approximately 1 second of residence time of sorbent in contact with potassium hydroxide vapor at high temperature, not including the residence time at lower temperature in the filter housing downstream. The reactor temperature was measured by a thermocouple adjacent to the tip of the sorbent injector, near the middle of the reactor. The vaporizer temperature was measured by a thermocouple in the space between the vaporizer heater and the outside of the vaporizer chamber. The filter temperature was taken to be the average of readings by three thermocouples spaced at equal angles around the outside surface of the filter element.

Approximately 43 g of KOH were charged in the vaporizer at the beginning of each run. After each run, the KOH remaining in the vaporizer was dissolved in water and analyzed for potassium. The KOH feed rate was assumed to be the loss in potassium hydroxide from the vaporizer divided by the run time. Similarly, the sorbent feed rate was calculated from the change in weight of sorbent in the fluidized bed divided by the run time.

In Run No. 1, the reactor temperature was set at 1740 °F, near the temperature of raw gas from the entrained flow gasifier exit at the PSDF. In spite of concern that the gas leaving the reactor would be overcooled while passing through the region of the flanges connecting the reactor to the filter housing, the temperature at the filter was higher than the target of 740 to 800 °F. The reactor temperature was lowered to between 1450 and 1480 °F (still a reasonable temperature for syngas upstream of a candle filter in a hot-gas cleanup system) in subsequent runs, to bring the filter temperature into the desired range.

In Run No. 1, the vaporizer temperature was set at 1240 °F, the value, based upon the analysis presented earlier. A potassium concentration of 100 ppmv was expected in the gas entering the reactor. However, the KOH was delivered at a much higher rate than anticipated. In fact, the entire 43 g of KOH initially charged to the vaporizer was delivered over the 8-hour run. The observation of a fine particle fume in the jet of exhaust gas leaving the candle filter indicated that much of the potassium was present as a vapor species under the conditions at the filter (i.e., 895 °F). Another filter was installed on the exhaust to collect the fume. This filter quickly clogged, and some of the material on the filter burst into flame, when the housing was opened, suggesting that the vapor species condensed and deposited there may have been elemental potassium.

Table 2. Experimental Conditions.

Run No.	Date	Reactor Temp. (°F)	Vaporizer Temp. (°F)	Filter Temp. (°F)	Vaporizer Flow (scfh)	Dilution Flow (scfh)	Sorbent Carrier Flow (scfh)	KOH Feed Rate (g/h)	Sorbent ^a Feed Rate (g/h)	Ratio K to sorbent (mol/mol)
1	12/13	1740	1240	895	4.5	4.5	0.8	5.4	0.0	$\rightarrow\infty$
2	12/19	1470	1125	746	4.5	4.5	1.6	1.8	0.14	60
3	12/28	1480	900	770	4.5	4.5	1.6	5.6	0.24	106
4	1/5	1490	900	797	4.5	4.5	1.6	2.4	0.0715	150
5	1/10	1450	800	743	4.5	4.5	1.6	1.08	0.0285	170
6	1/16	1480	600	748	4.5	4.5	1.6	2.8	0.080	160

a. The sorbent was kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

The NASA Chemical Equilibrium with Applications (CEA) computer code [34] was run to determine the equilibrium composition of a system initially consisting of KOH in the presence of N_2 . The CEA code calculation did not predict the presence of any vapor species other than KOH and the KOH dimer, $(KOH)_2$, in significant concentration at any temperature in the range from 600 to 1800 °F, and the sum of the mole fractions, $KOH + 2(KOH)_2$, predicted by the CEA code was in approximate agreement with the vapor pressure for KOH shown in Figure 4. Therefore, the high metal feed rate is so far unexplained. One possibility is that radiative heat from the furnace may have evaporated additional metal from the reservoir.

In subsequent runs, the temperature of the vaporizer was lowered, first to 1125 °F, then to 900, 800, and 600 °F, in attempts to achieve 100 ppmv of potassium in the flow through the reactor. At the lower temperatures, no fume was observed in the exhaust from the filter, but the rate of delivery of potassium from the vaporizer was still higher than expected for all of the conditions investigated. A plot of the observed potassium flow rate from the vaporizer (based on the initial weight of KOH charged to the vaporizer and the potassium remaining in the vaporizer, at the end of the run), as a function of the vaporizer temperature, is shown in Figure 10.

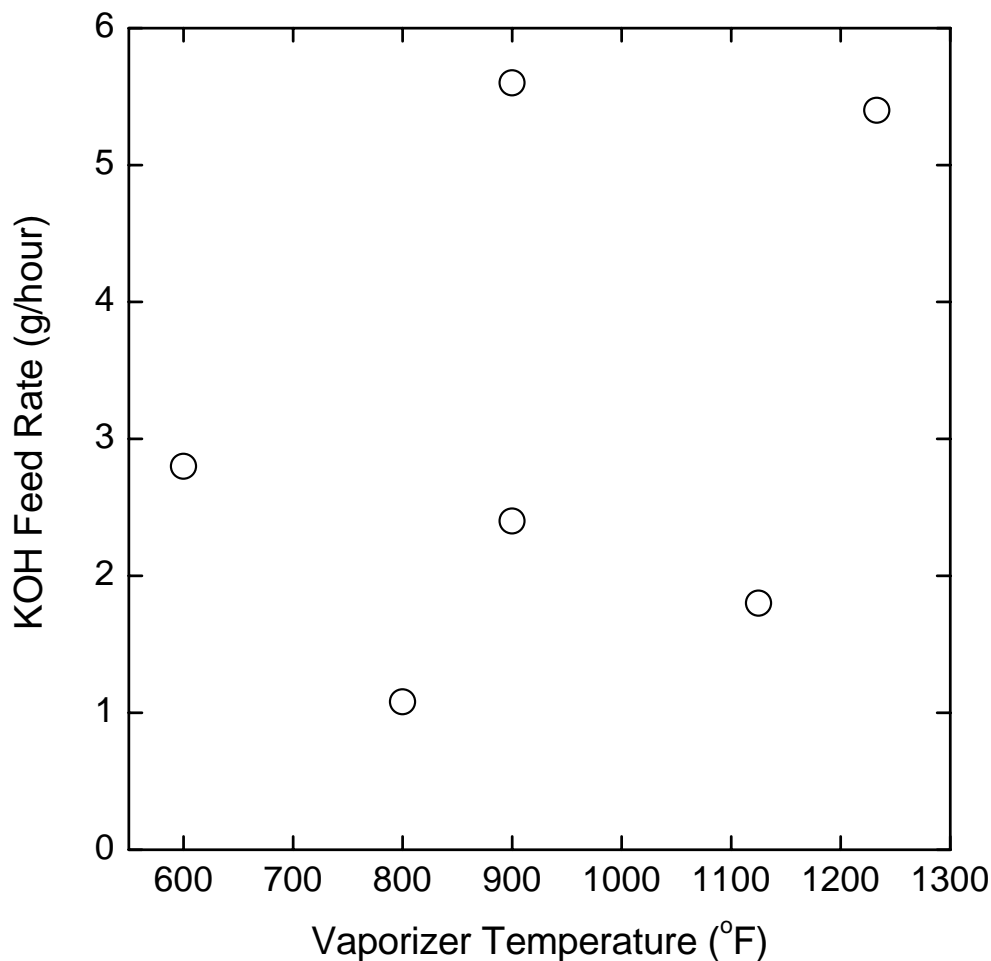


Figure 10. Flow rate of potassium hydroxide delivered by the vaporizer, as a function of the temperature indicated by the thermocouple in the flow near the top of the vaporizer.

Even at the lowest temperature, 600 °F, which is below the melting temperature of KOH (681 °F), the potassium feed rate was much higher than the target of 0.065 g/h that would have been stoichiometric with a feed rate of 0.150 g/h of kaolinite (2 moles of K per mole of kaolinite). There is little or no correlation between the temperature in the vaporizer heater and the rate at which potassium hydroxide was delivered. It is difficult to explain the unexpectedly high rates of delivery of KOH under these conditions, other than to suggest that the temperature at the surface of the molten KOH is somehow independent of the temperature indicated by the thermocouple in the space between the heater and the outside of the vaporizer. Additional thermocouples are needed to better characterize the temperature distribution in the KOH itself.

The feed rate of kaolinite from the fluidized bed made of stainless steel tubing was not as consistent or reproducible as it had been from the prototype made from polystyrene tubing. The target feed rate was 0.150 g/h. The actual feed rates, averaged over the durations of the runs, varied from 0.0285 to 0.24 g/h. The performance of the stainless steel fluidized bed feeder needs to be optimized with respect to pre-drying the powder sorbent, the mass of the bed, preconditioning to remove fines, the flow rate of fluidizing gas, the flow rate of air to the pneumatic vibrator fastened to the tube, and the height of freeboard above the bed.

RESULTS AND DISCUSSION

Much of the effort on this project has gone into designing and building a slipstream reactor that was capable of reproducing conditions consistent with hot-syngas cleanup systems. The journey through this effort has been aptly described in the EXPERIMENTAL section of this report. As discussed, a reactor was devised whereby realistic sorbent/particle interactions could take place at the correct temperature and residence time as would be expected for sorbent injection upstream of a candle filter. Furthermore, the reactor design allows for the complicated but important coupling of dispersed sorbent interaction with metal vapor in the hot syngas and sorbent collection on candle filter elements immediately afterward, at much lower temperatures and for much longer times. Because of the multiple interacting processes involved in the application of this technology to real gasifiers and hot-gas cleanup systems, these processes must be coupled in order to examine the pertinent mechanisms involved.

There are two main responses that this hot-syngas sorbent technology must consider, namely (1) the ability of the sorbent to scavenge metal from the syngas, thus preventing it from passing through the filter or contacting the filter in a harmful form, and (2) the sorbents overall ability to protect the filter, by avoiding eutectic melting, by preventing eutectic melting of other ash components or the filter itself, and by scavenging harmful and potentially corrosive components in the syngas. The reactor design and tests begun under this project can produce the very information needed.

Unfortunately, budget cuts have severely crippled this project, and only the initial testing has been accomplished before the tests had to be halted. However, some encouraging initial results have been obtained, as will be shown, and the project has been halted in place and the equipment has been setup so that it can be quickly and inexpensively used to resume and complete this important work, as soon as funding is restored or additional sources of funding obtained.

Slipstream Test Results

The testing that was accomplished with the available funding was with the complete reactor assembly installed in the slipstream facility at the PSDF, using pure nitrogen for all gas flows, potassium hydroxide as the metal vapor in the system, and Burgess-40 kaolinite powder sorbent as the high-temperature sorbent tested. While Burgess-40 is reagent-grade sorbent, it has very similar properties to much less expensive waste-derived sorbent. Yet, the kaolinite is convenient to allow the test of a known structure, without convoluting effects from other components that exist in waste-derived sorbent. With an understanding of the mechanisms contributed from the more pure components of the sorbent, it will be possible to construct the most effective designer sorbent for the particular application, and yet keep the sorbent inexpensive.

As discussed in the experimental section, the new reactor design produced an environment that replicated the conditions of existing hot-syngas cleanup systems. The metal vaporizer was effective at producing entrained potassium vapor in the reactor gas stream, the sorbent feeder was able to disperse powder sorbent at the desired distance and residence time in the reactor, the reactor was kept at the temperature desired, the candle filter did effectively collect the injected sorbent and captured metal without clogging, and the filter and filter housing were maintained at the desired temperature.

Table 3 contains the composition of material found on the filter cake for six different tests, assuming that all the metals were in the oxide form and that the remaining mass was water. Kaolinite has a significant amount of oxygen and water in its crystal matrix. Although potassium hydroxide was the form of potassium vaporized in the furnace, the potassium form most readily reported in the aluminosilicate phase-diagram literature is the oxide form (i.e., K_2O).

Table 3. Material collected on the candle filter.

Test Run	Total Mass (g)	K_2O (wt%)	Al_2O_3 (wt%)	SiO_2 (wt%)	H_2O (wt%)	Si/Al (molar ratio)
1	0.1398	41.08	15.31	---	---	---
2	0.2711	21.56	25.89	31.29	21.27	1.02
3	0.0124	10.60	36.09	30.64	22.67	0.72
4	0.1509	15.18	34.58	41.57	8.67	1.02
5	0.0422	11.32	62.73	41.36	(15.47)	0.56
6	0.0653	5.78	23.24	46.50	24.48	1.69

For condition 1, no sorbent was injected, only KOH. As shown in Table 3 for Run 1, the material collected on the filter was found to possess a large quantity of aluminum oxide. The material on the filter was also analyzed for iron, but none was found. The filters are composed of iron aluminide, and apparently the vaporized potassium reacted directly with the filter element, leaching the aluminum from the iron aluminide filters, while leaving the iron in place. This is consistent with the metal activity series, which places potassium near the top of the active metals, aluminum below, and iron well below aluminum.

Other than condition 1, where no sorbent was fed, the filter cake had approximately 30 wt% of both Al_2O_3 and SiO_2 . A significant exception to this was Run 5, for which the Al_2O_3 concentration was measured at ~63 wt%. This particular run was also peculiar, because assuming that all of the metals form oxides (which is how the data in Table 3 are represented), the sum of the potassium oxide, alumina, and silica add up to greater than 100% – hence the negative value for the water in the dust cake. If the alumina weight percentage for Run 5 was the same as for Run 4 (e.g., 34.58 wt%), then the water wt% would be approximately +13 wt% for Run 5. It is possible that for condition 5 some of the potassium reacted with the filter element, forming potassium aluminates. However, for the other samples the wt% of alumina suggests that the capture was primarily on sorbent, thus demonstrating that the sorbent protected the filter from reaction with the metal.

Table 3 contains the Si/Al molar ratio of each filter cake. A molar ratio indicative of kaolinite (or meta kaolinite) would be 1.0. As shown, the molar ratios are consistent with this, other than conditions 1 and 5. Condition 5 contained almost twice as much Al as Si. Some scatter in the

data is obvious for the other conditions, which may have been caused by the difficulty in chemically analyzing the small samples.

The filter cake from each test was also analyzed for soluble and insoluble Al, Si, and K. It has been shown [35-37] that meta-kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), and metal captured in the aluminosilicate crystal structure (i.e., $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) are not water soluble. However, unbound potassium components (i.e., K_2O , K, and KOH) and most potassium silicates are soluble in water. Some potassium aluminates are soluble, but the longer these compounds bake, the more likely it is that they will transform into an insoluble form. Since the sorbent baked on the candle filters for a number of hours during each of these experiments, most of the alumina and potassium aluminates (if there were any) should have been insoluble.

Figure 11 contains a plot of the insoluble metals found in the filter cake of each test run, plotted as a function of the sorbent/metal equivalence ratio measured in respective filter cakes. The amount of meta-kaolinite collected in each filter cake was calculated both based on the amount of silicon found in the cake and subsequently by the quantity of aluminum found in the filter cake. Both methods used $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_3$ as the formula for meta-kaolinite (i.e., calcined kaolinite).

As shown in Fig. 11, very little soluble silicon or aluminum was found in the filter cake for any of the tests, suggesting that few if any soluble metal/sorbent reaction products were formed. This is also evidence that the meta-kaolinite crystal structure remained in tact, and that little if any melting of the particles occurred. Furthermore, as little as 50% and as much as 85% of the potassium was insoluble for all filter cakes, suggesting that significant reactive capture of potassium occurred.

Nevertheless, the data in Fig. 11 indicates significant sorbent utilization. Sorbent/metal equivalence ratio metal-capture-limit lines in Fig. 11 indicate the maximum percentage of metal that can be captured based on four different equivalence ratios, $\phi = 1/1, 1/2, 1/4, \text{ and } 1/8$. Maximum in-flight capture of sodium and lead by kaolinite in vitiated post-flame air was previously published as being limited to an equivalence ratio of 1/1 [39, 40]. Subsequently, it was shown that the limit based on $\phi = 1/2$ and even 1/4 could be reached for the same conditions, if sorbent melting occurred, where the aluminosilicate crystalline structure decomposed to allow the formation of separate silicates and aluminates [1-3, 5].

Even though the current investigation considers K_2O products, a different metal oxide than the PbO and Na_2O considered in the previous work, it is likely that the mechanisms involved will be similar and the maximum utilization limits should apply to all these types of metal. Nevertheless, unlike the previous investigation, metal capture percentages were obtained in this work, as shown in Fig. 11, that reached equivalence ratios as high as 1/8, and this without any melting of the sorbent matrix.

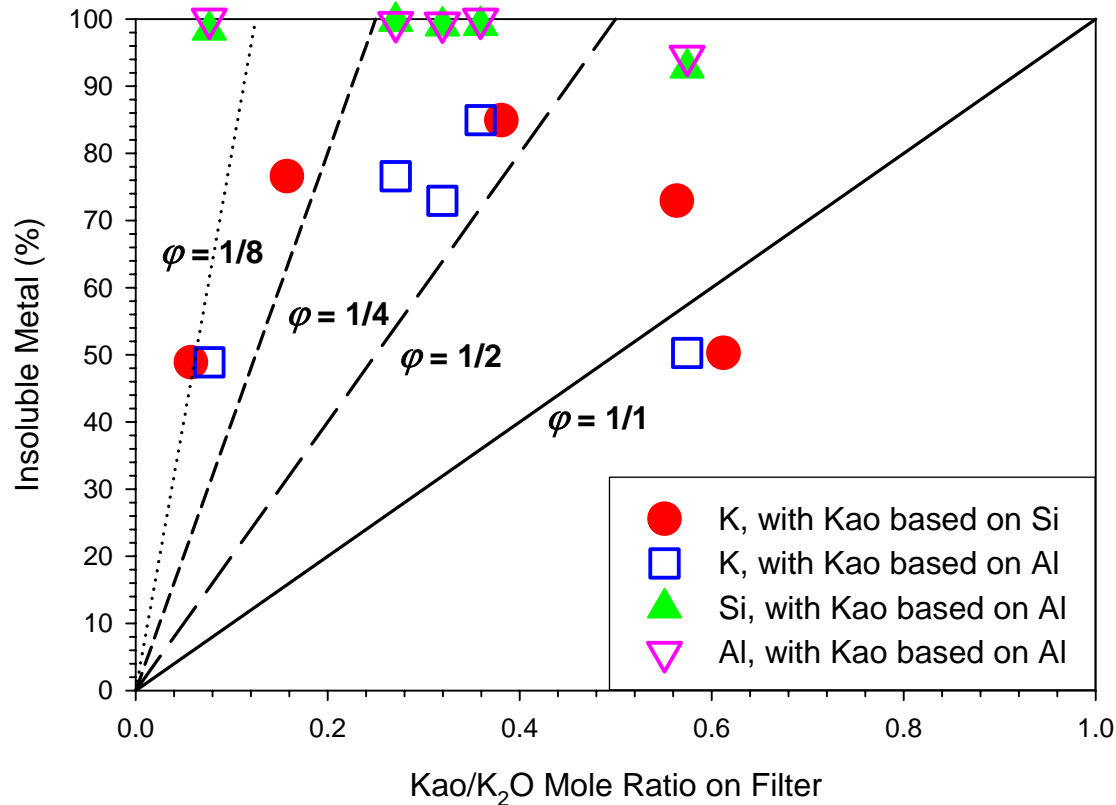


Figure 11. Insoluble metals found on the filter cake, as a function of Kaolinite/K₂O ratio.

The high capture percentages (i.e., insoluble metal %) observed (see Fig.11) at low equivalence ratios was encouraging. However, extremely high metal-removal percentages (i.e., 99.999% removal) were not obtained. On the other hand, sorbent was not allowed to build up on the filter before metal vaporization and injection began. Therefore, higher capture percentages of the metal may be possible in the full-scale application. Also, a maximum in metal capture (insoluble metal collected) of about 85% is shown in Fig. 11 with an equivalence ratio of approximately 1/4. The validity of this maximum will need to be investigated further.

Figures 12 and 14 show SEM images of the potassium collected on the filter without any sorbent injection, from condition 1. As shown in the EDS spectra of Figures 13 and 15, the material was primarily aluminum and potassium, indicating that the potassium reacted with the candle filter element to form potassium aluminates.

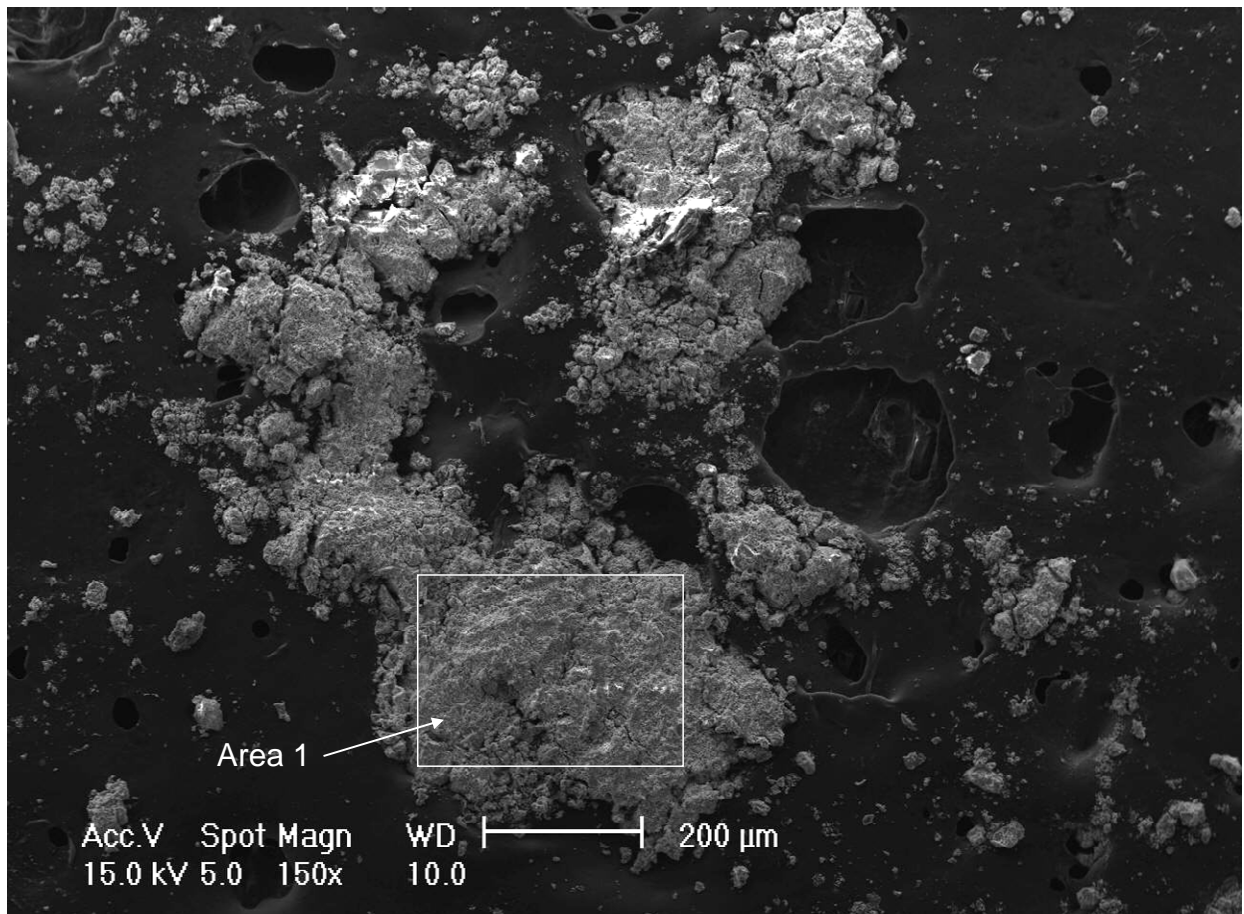


Figure 12. First SEM of filter cake from condition 1.

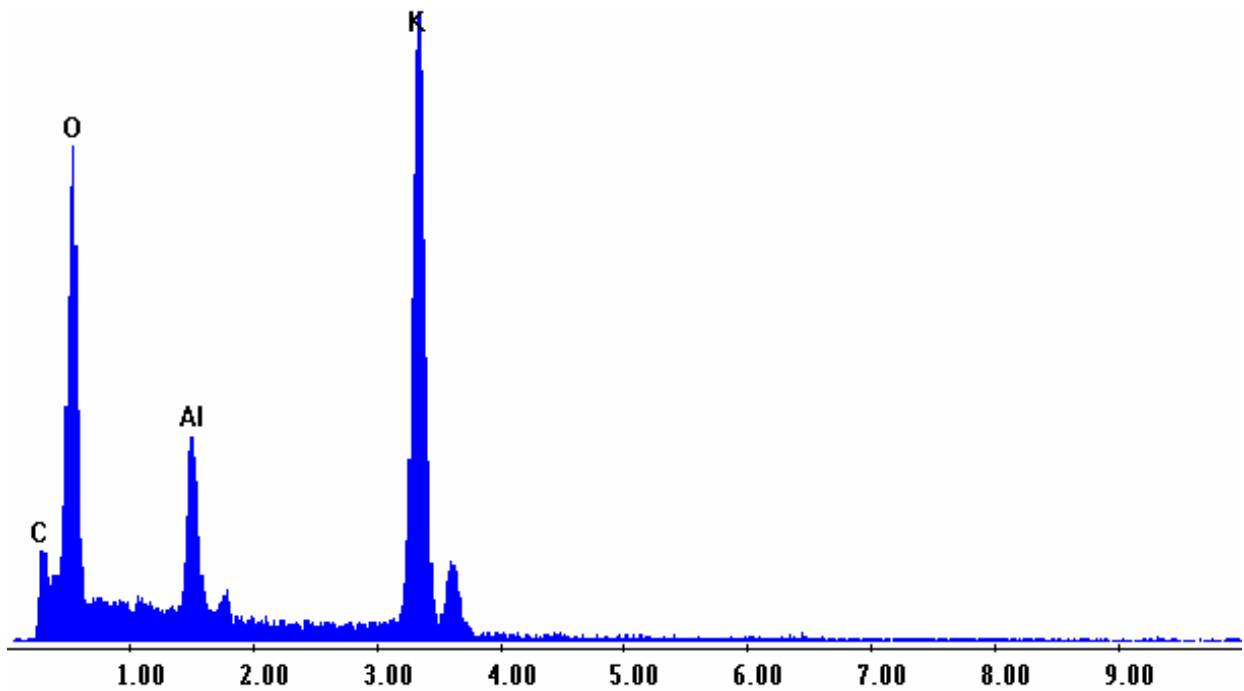


Figure 13. EDS spectra of Area 1 in Fig. 12.

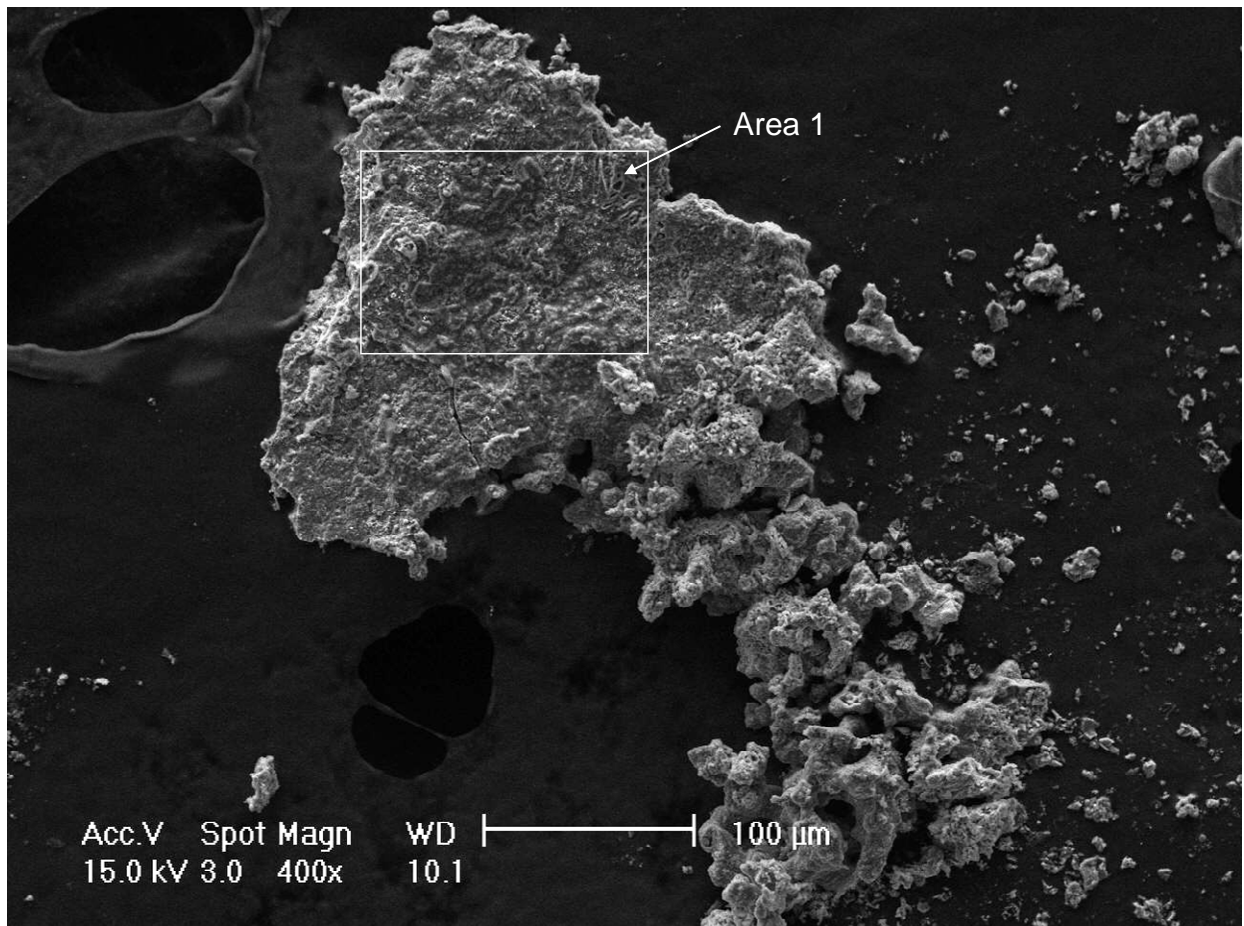


Figure 14. Second SEM of filter cake from condition 1.

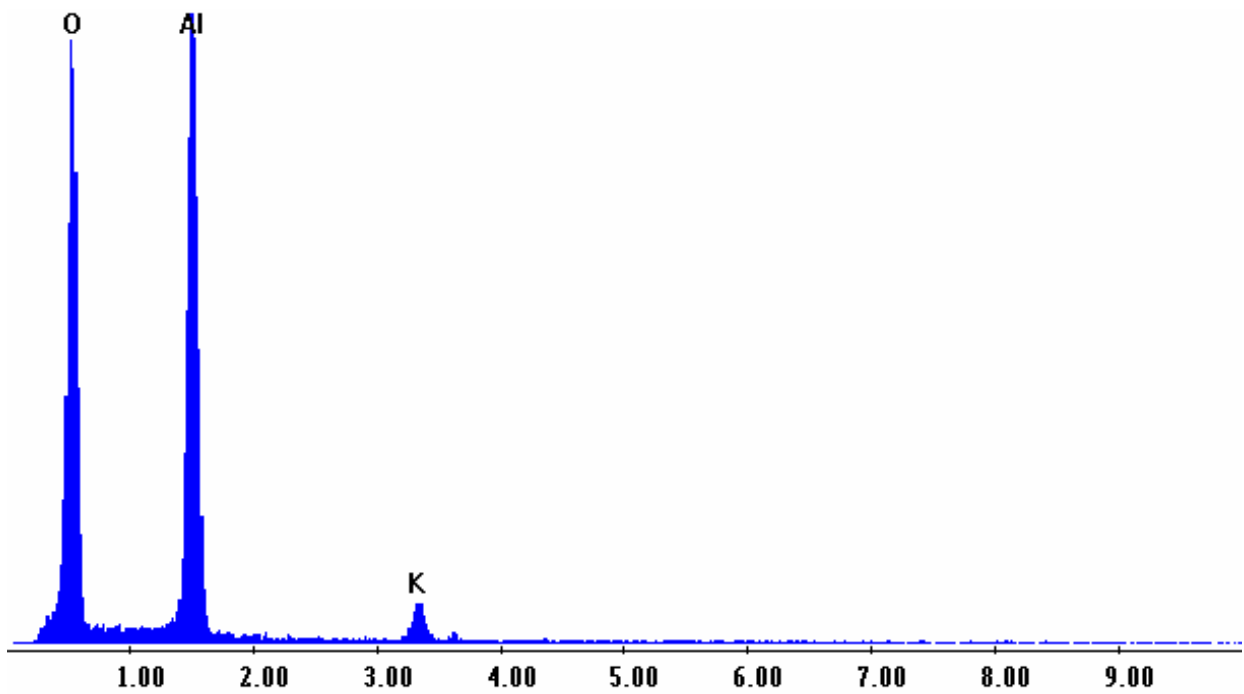


Figure 15. EDS spectra of Area 1 in Fig. 14.

The SEM images and EDS spectra of Figures 16 through 37, indicate that all of the sorbent/metal product particles were crystalline, and experienced little if any melting, an observation that is very consistent with the insolubility of aluminosilicate products in each filter cake. While the EDS results are primarily qualitative, there appeared to be equal amounts of aluminum and silicon present in each sample. Significant potassium capture was also confirmed.

The low equivalence ratios observed and the high sorbent utilizations combined with a lack of sorbent melting in the experiments conducted in this work is an exciting result relative to high-temperature sorbents for capturing metals from hot syngas. It is desirable to avoid eutectic melting of the sorbents, which potentially could significantly contribute to melting on the candle filters and clogging of the filter elements.

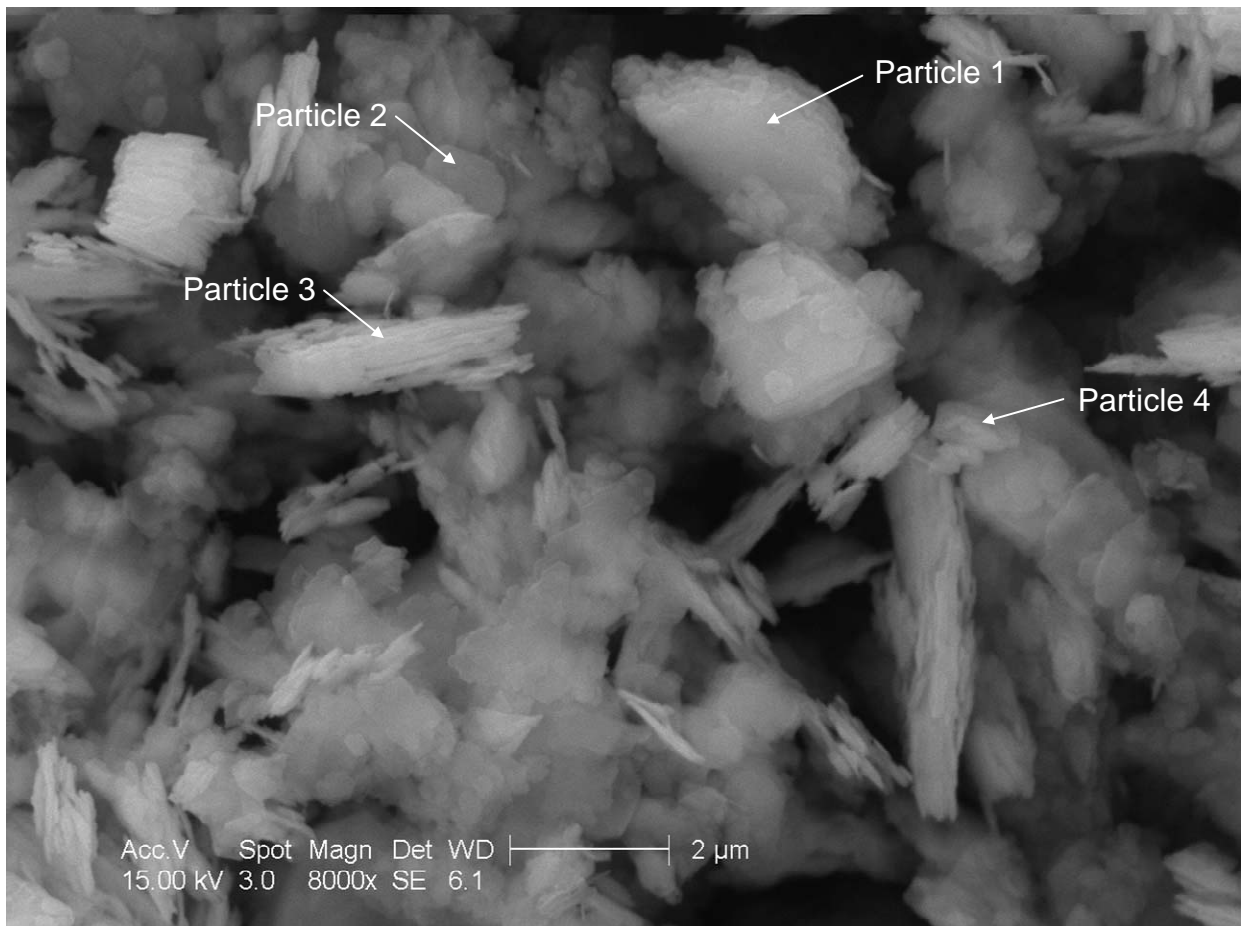


Figure 16. SEM of filter cake from condition 2, from dark area on filter.

Even for eutectic melting, the syngas temperatures probably need to be above 1500 °F. The gas temperatures in the main reaction chamber were intentionally kept below this temperature, for this reason. In addition to remaining crystalline, clearly non-melted sorbent/metal reaction products will help eliminate sticky filter cakes, filter clogging, and bridging between candles. The observation that high sorbent utilizations can be obtained without melting is a result that was previously unknown. This result may be associated with the ability of kaolinite clay powders to capture metals more efficiently over long periods of time, while in a dust cake on a filter than

while suspended in the gas phase for a few seconds [1-3, 5]. If this result is shown to hold up for other metals and multi-metal systems, then it is highly likely that high-temperature sorbents may be able to effectively remove unwanted semi-volatile metals and protect candle-filter elements economically.

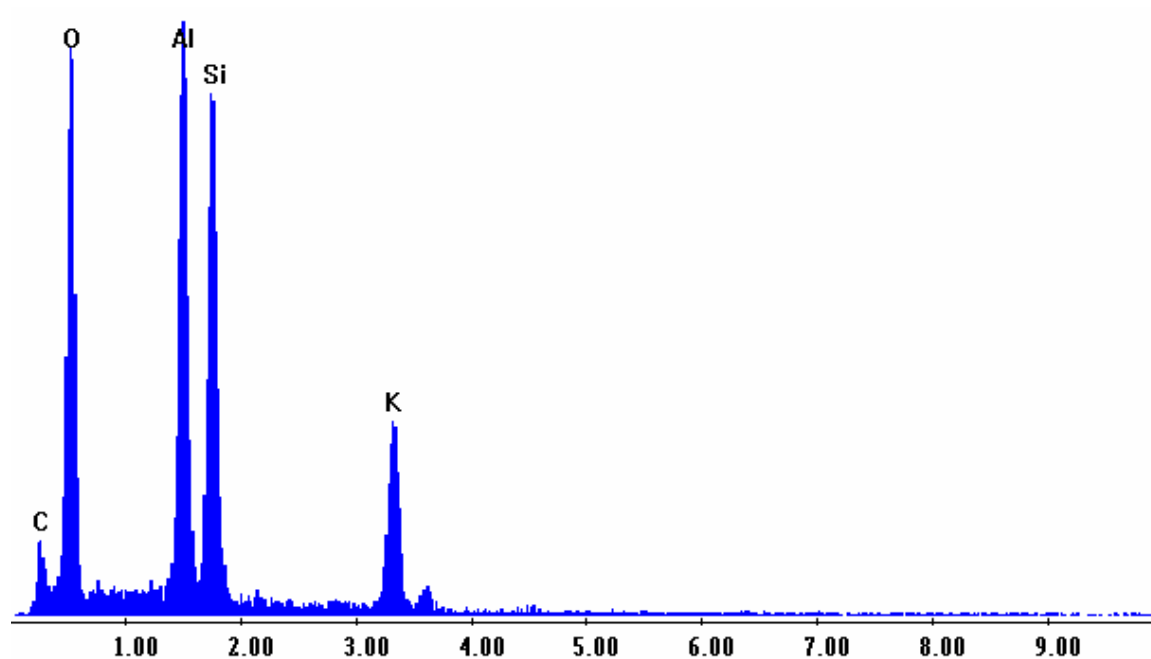


Figure 17. EDS spectra of Particle 1 in Fig. 16.

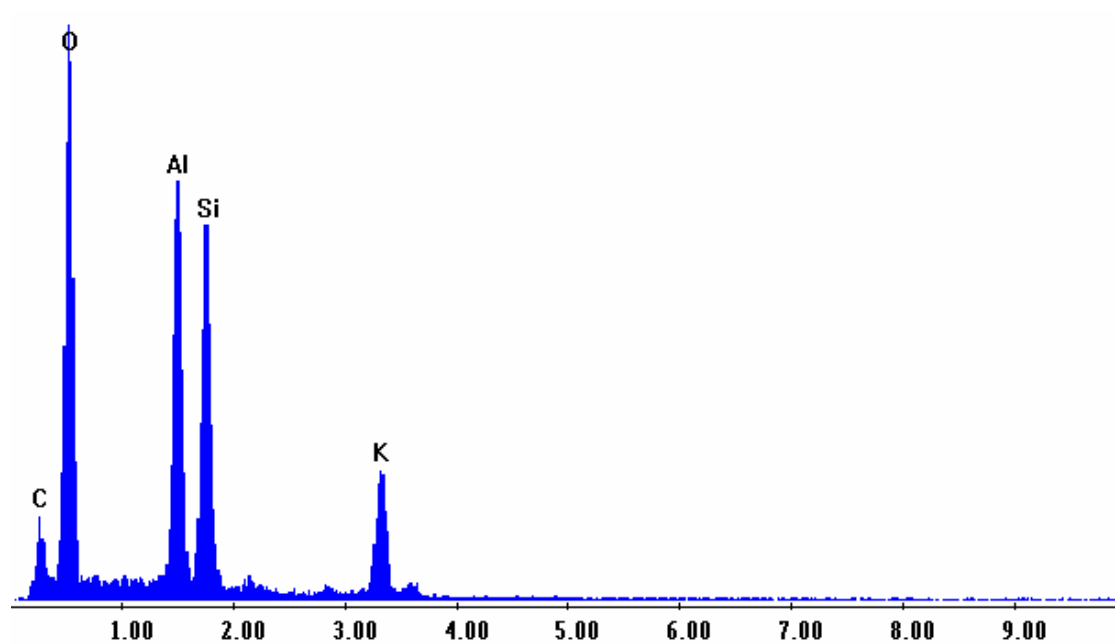


Figure 18. EDS spectra of Particle 2 in Fig. 16.

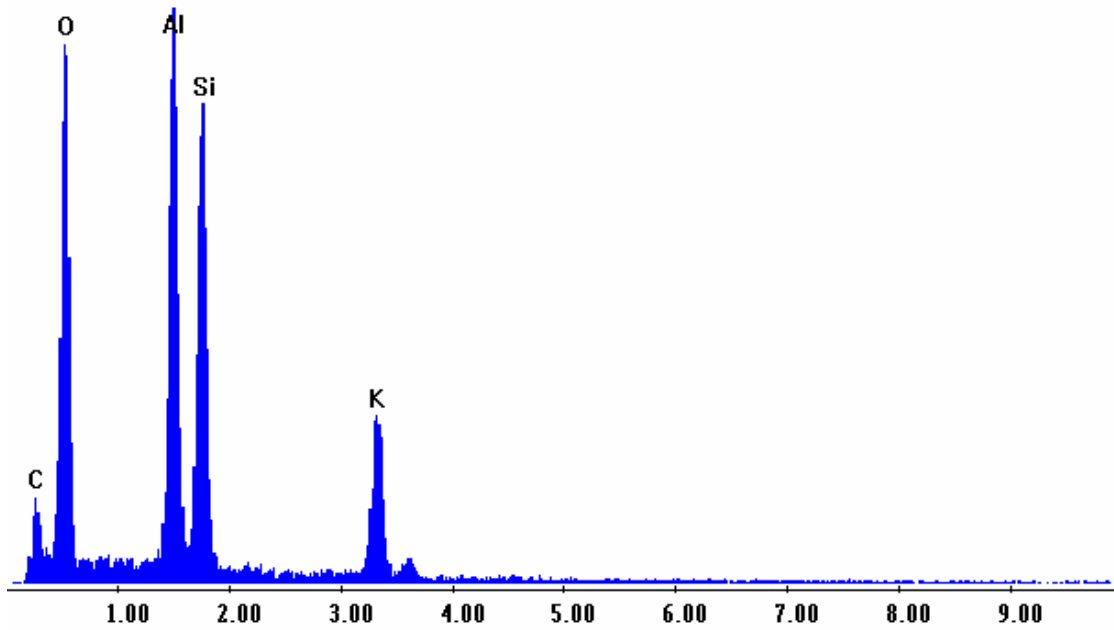


Figure 19. EDS spectra of Particle 3 in Fig. 16.

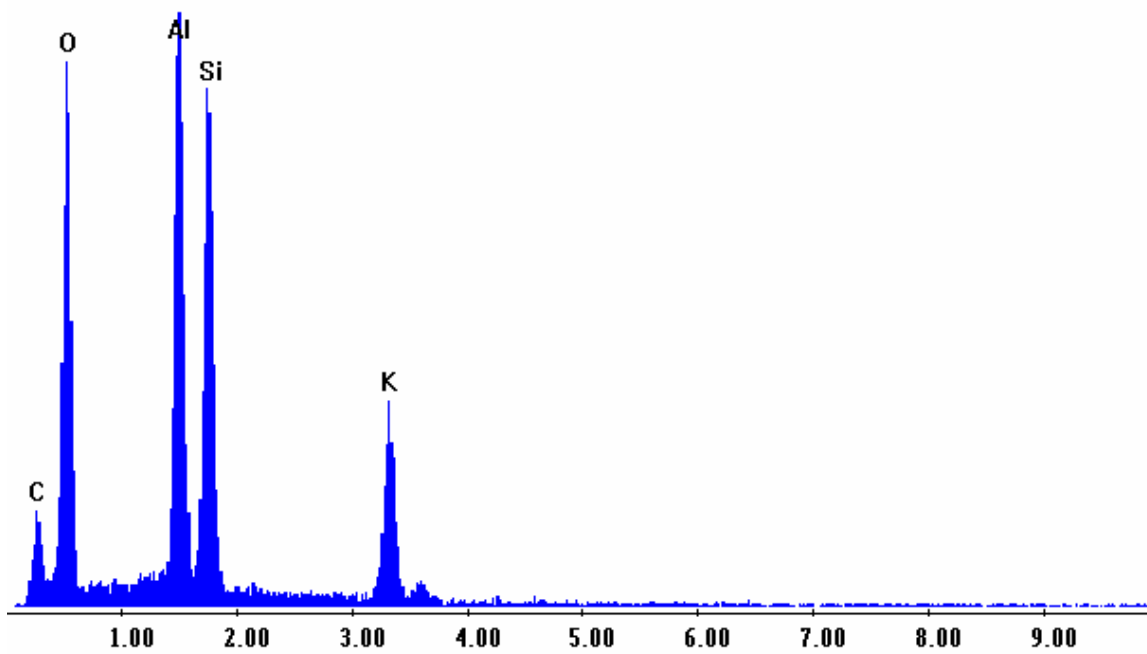


Figure 20. EDS spectra of Particle 4 in Fig. 16.

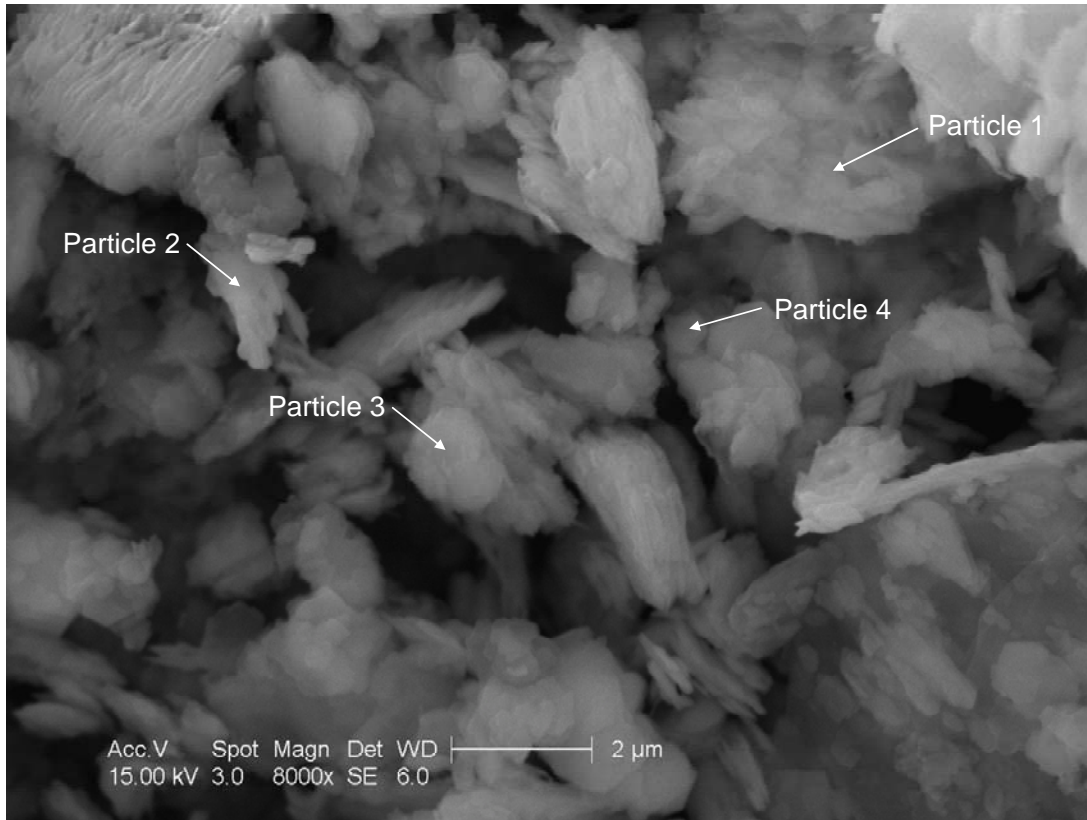


Figure 21. SEM of filter cake from condition 2, from light area on filter.

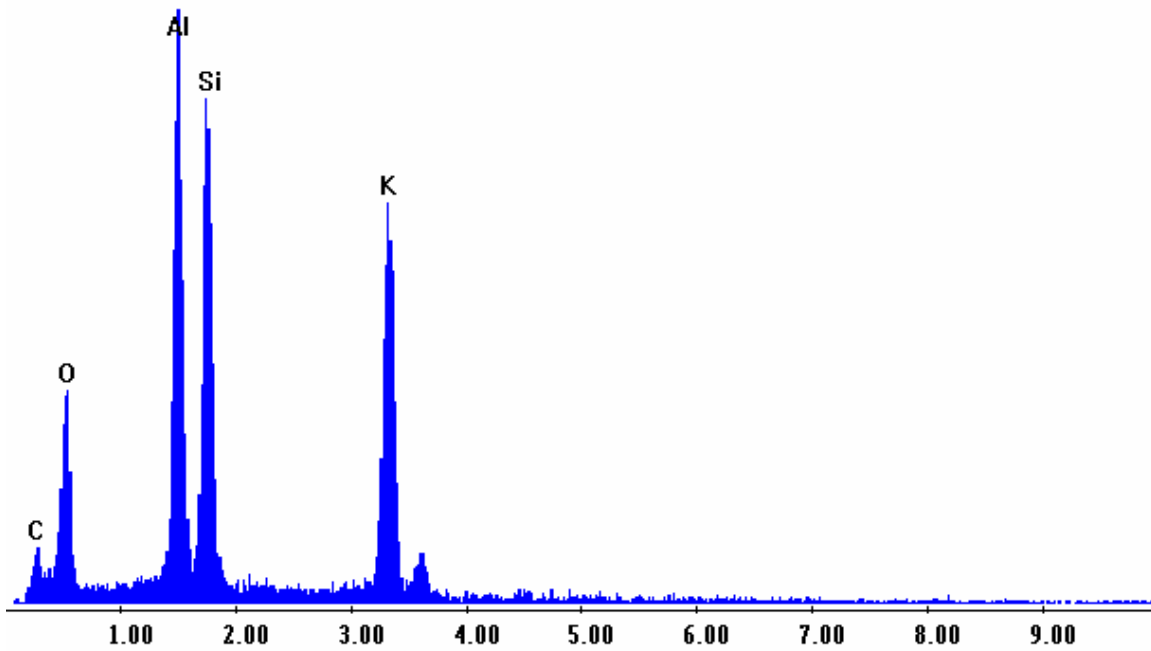


Figure 22. EDS spectra of Particle 1 in Fig. 21.

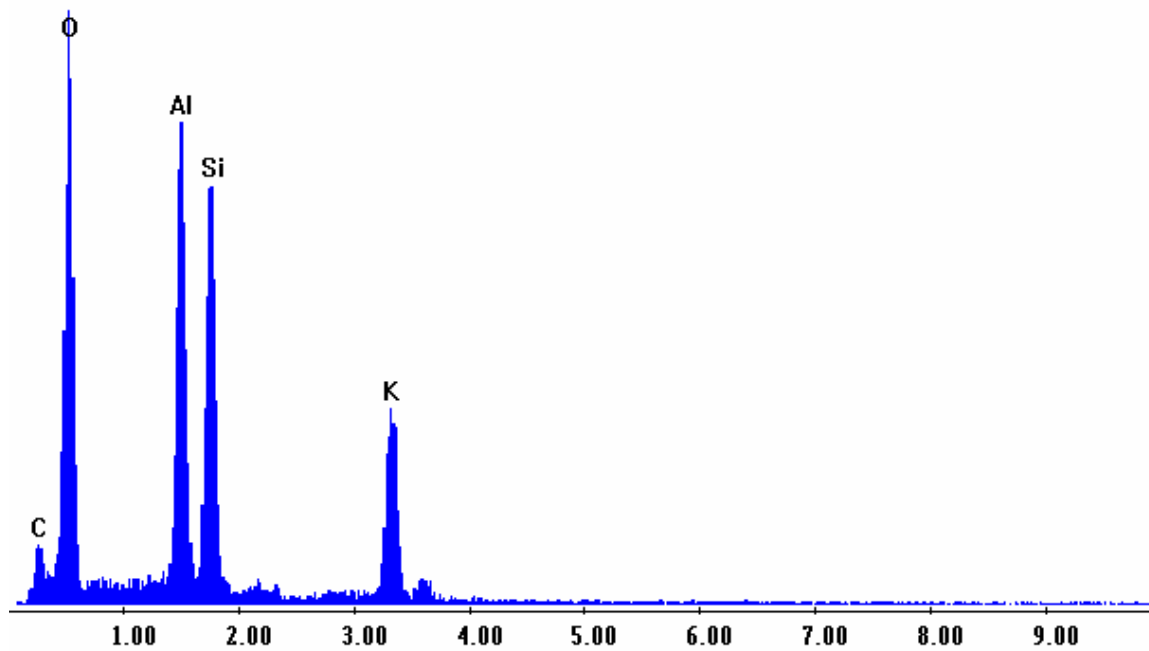


Figure 23. EDS spectra of Particle 2 in Fig. 21.

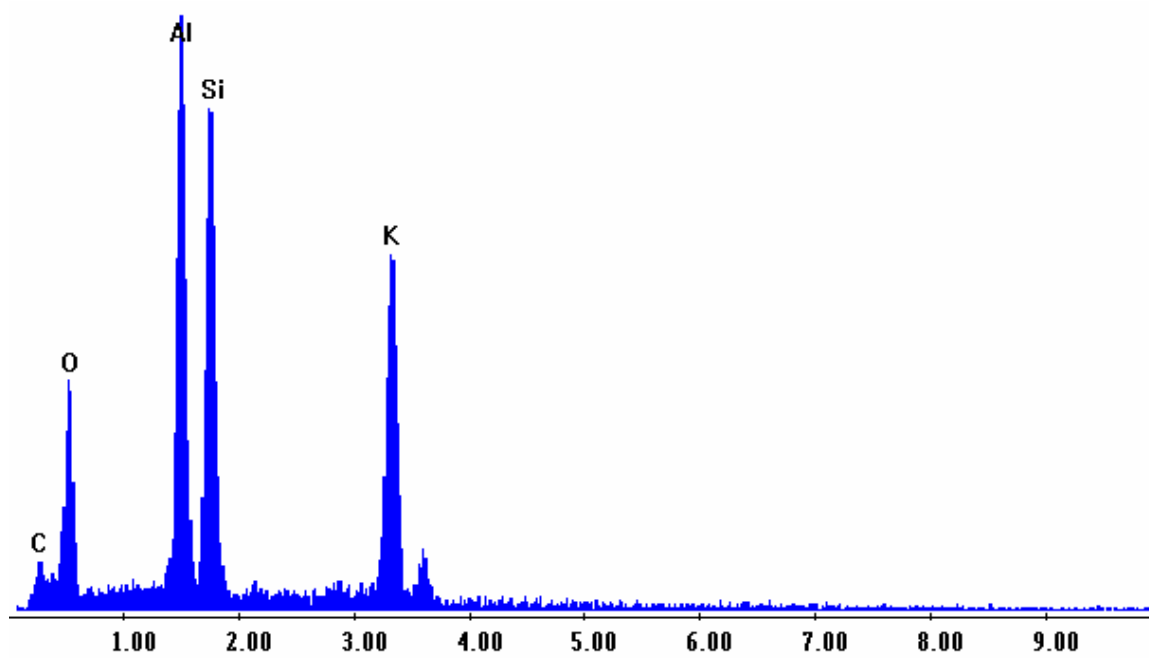


Figure 24. EDS spectra of Particle 3 in Fig. 21.

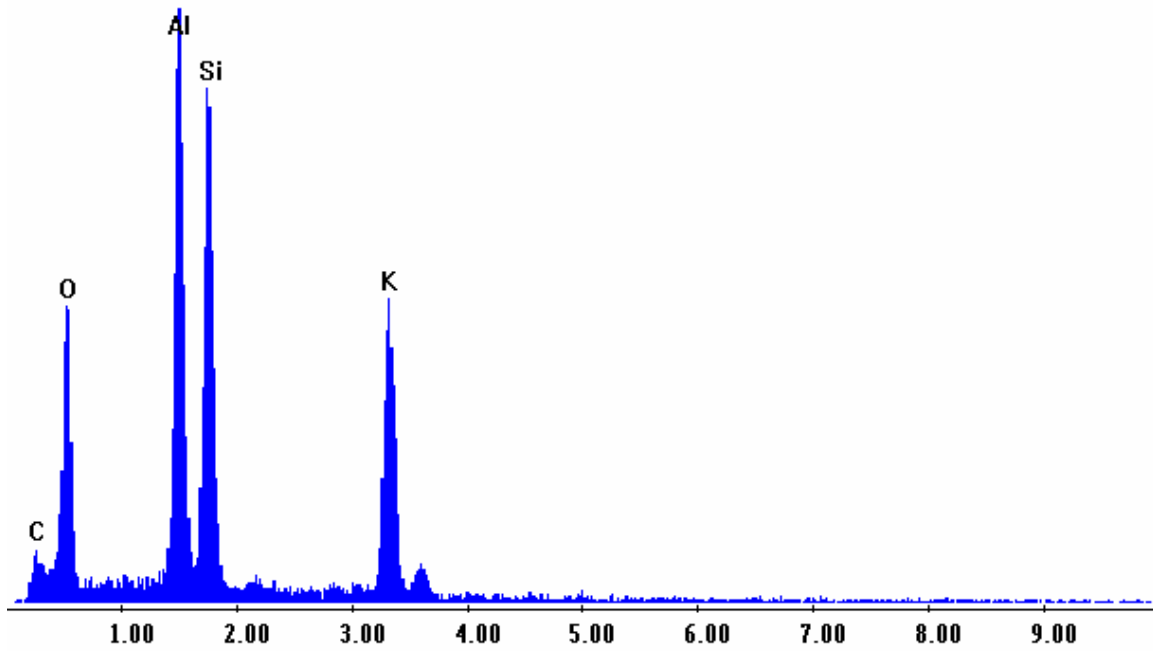


Figure 25. EDS spectra of Particle 4 in Fig. 21.

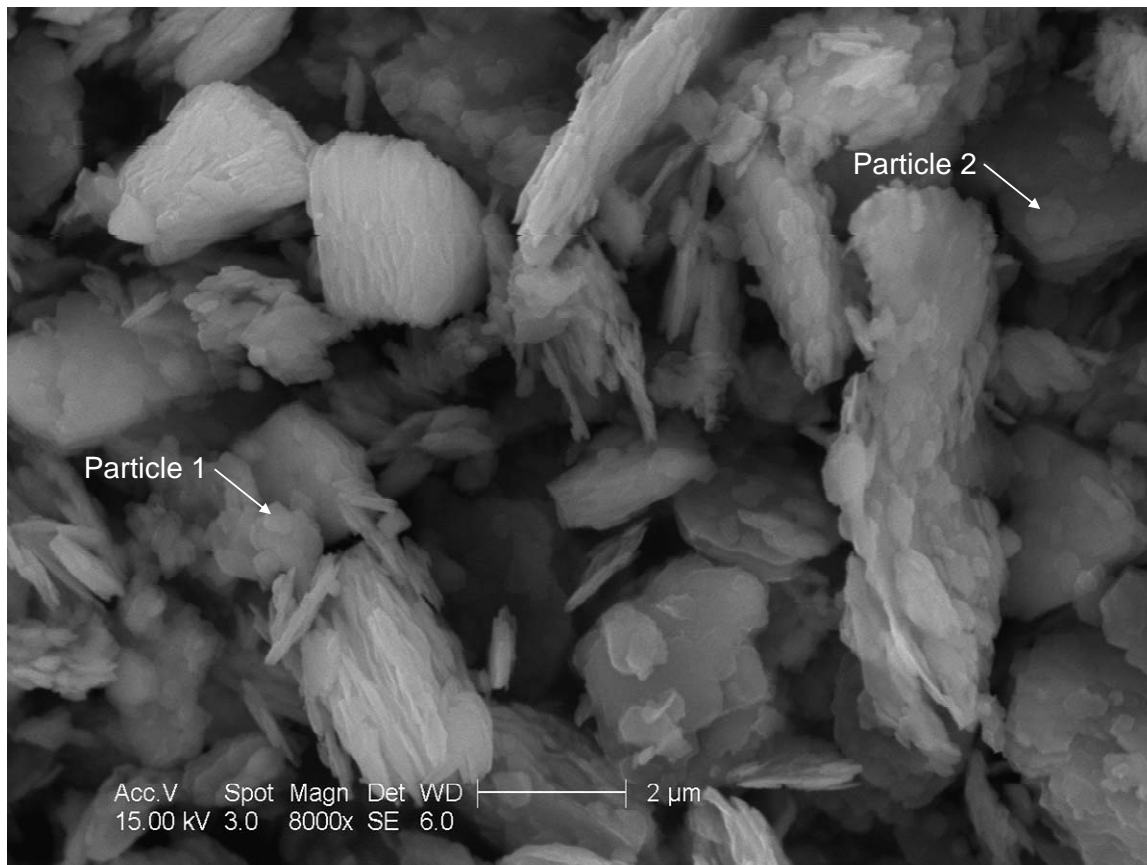


Figure 26. SEM of filter cake from condition 3, from dark area on filter.

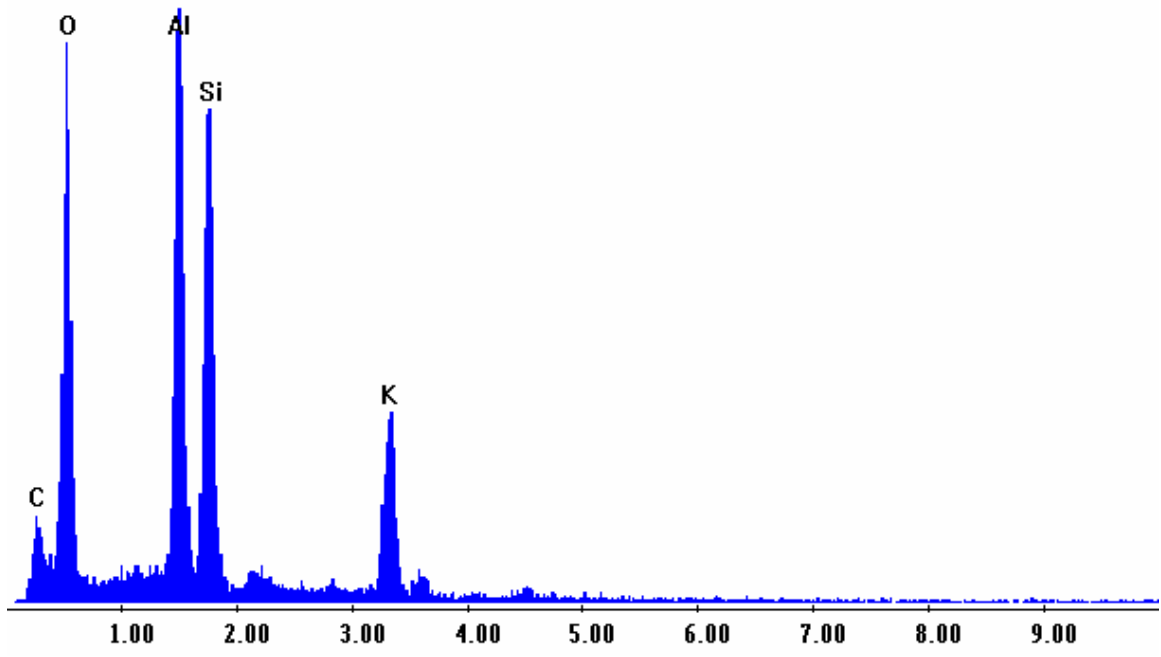


Figure 27. EDS spectra of Particle 1 in Fig. 26.

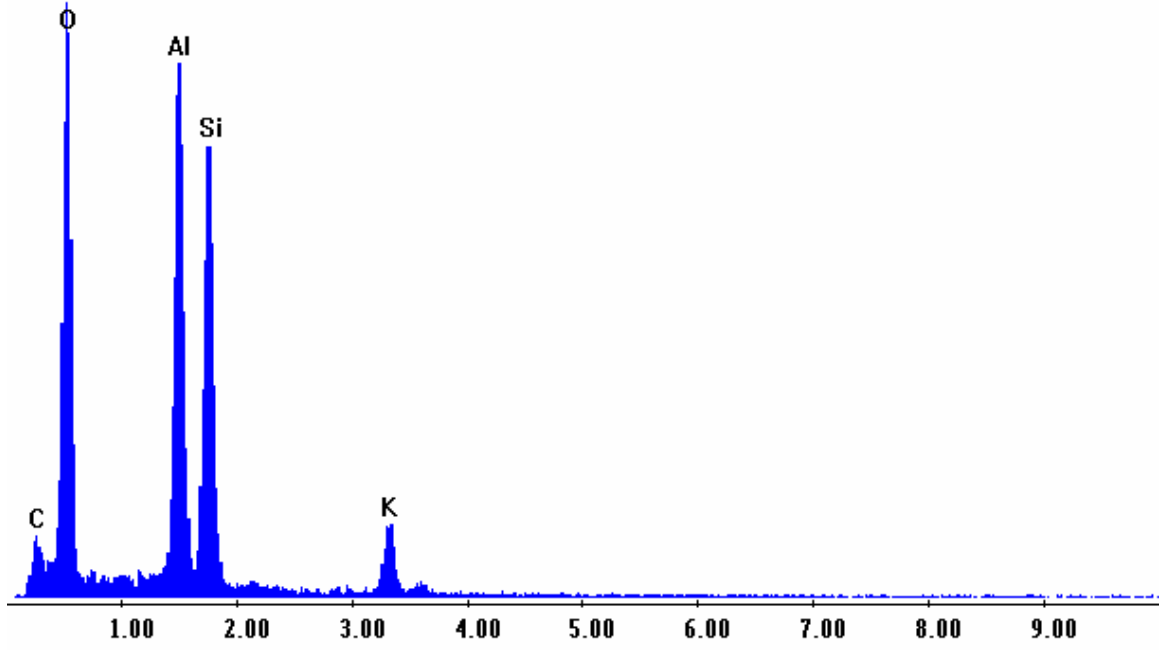


Figure 28. EDS spectra of Particle 2 in Fig. 26.

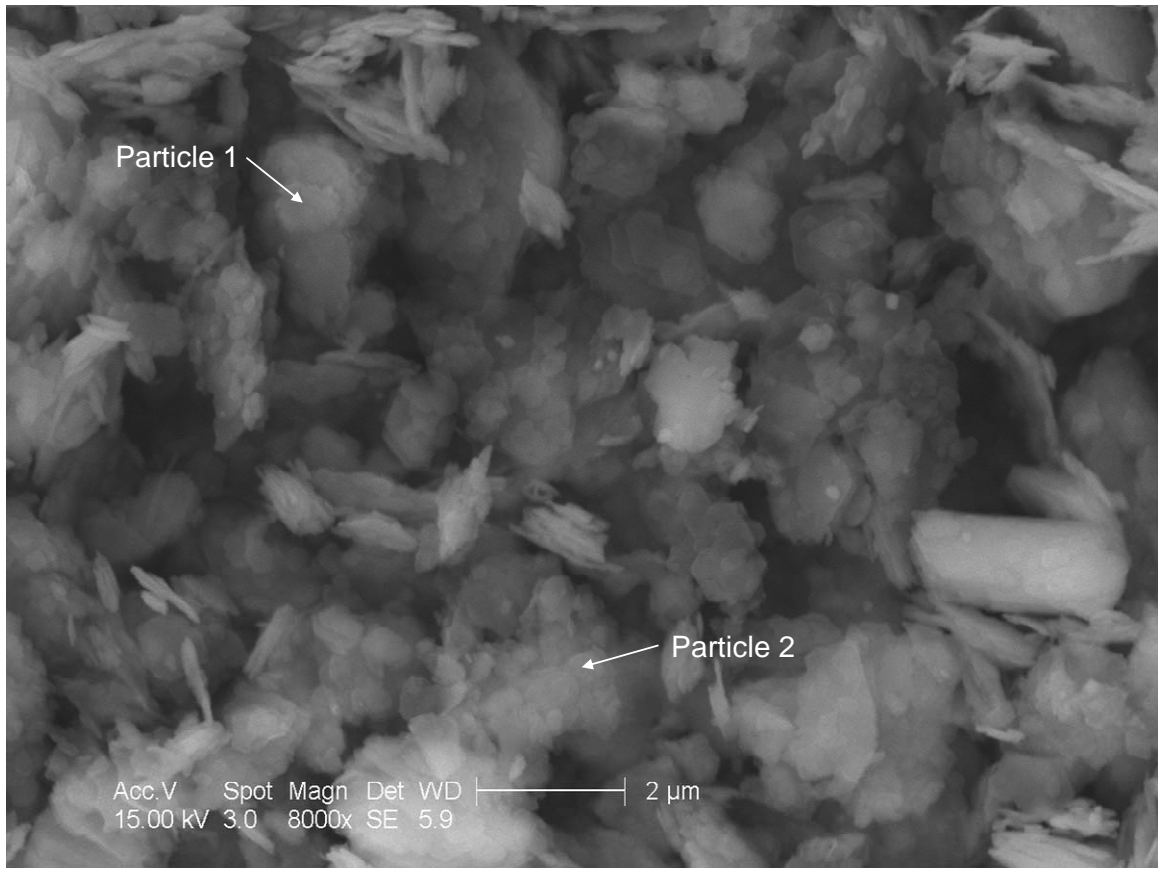


Figure 29. SEM of filter cake from condition 3, from light area on filter.

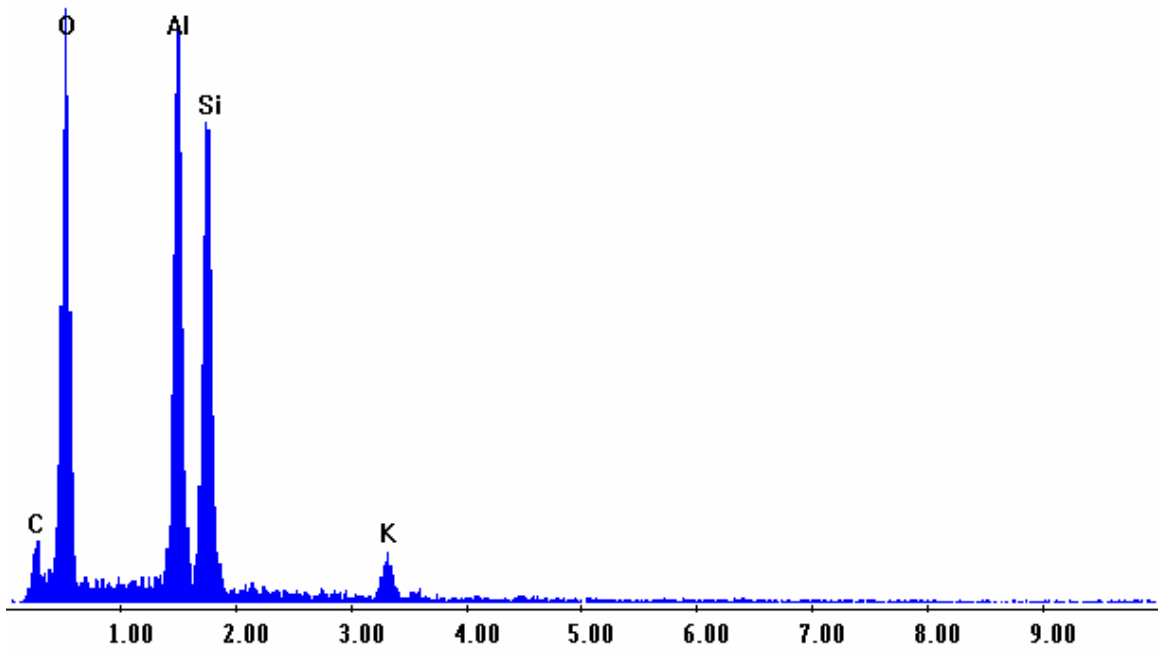


Figure 30. EDS spectra of Particle 1 in Fig. 29.

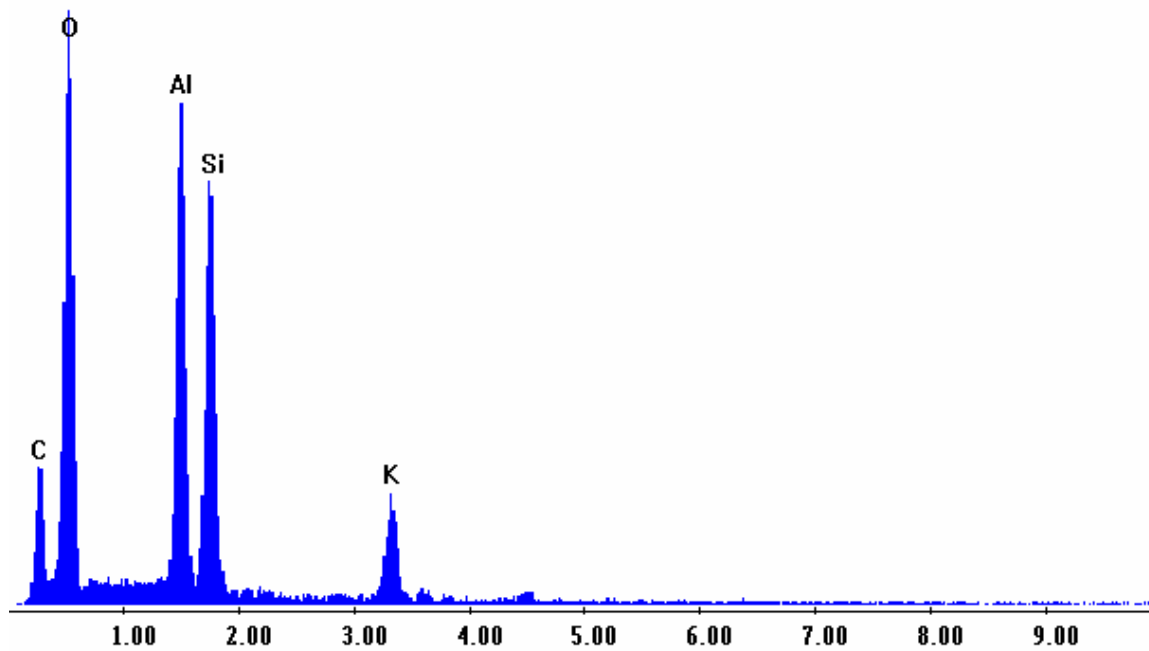


Figure 31. EDS spectra of Particle 2 in Fig. 29.

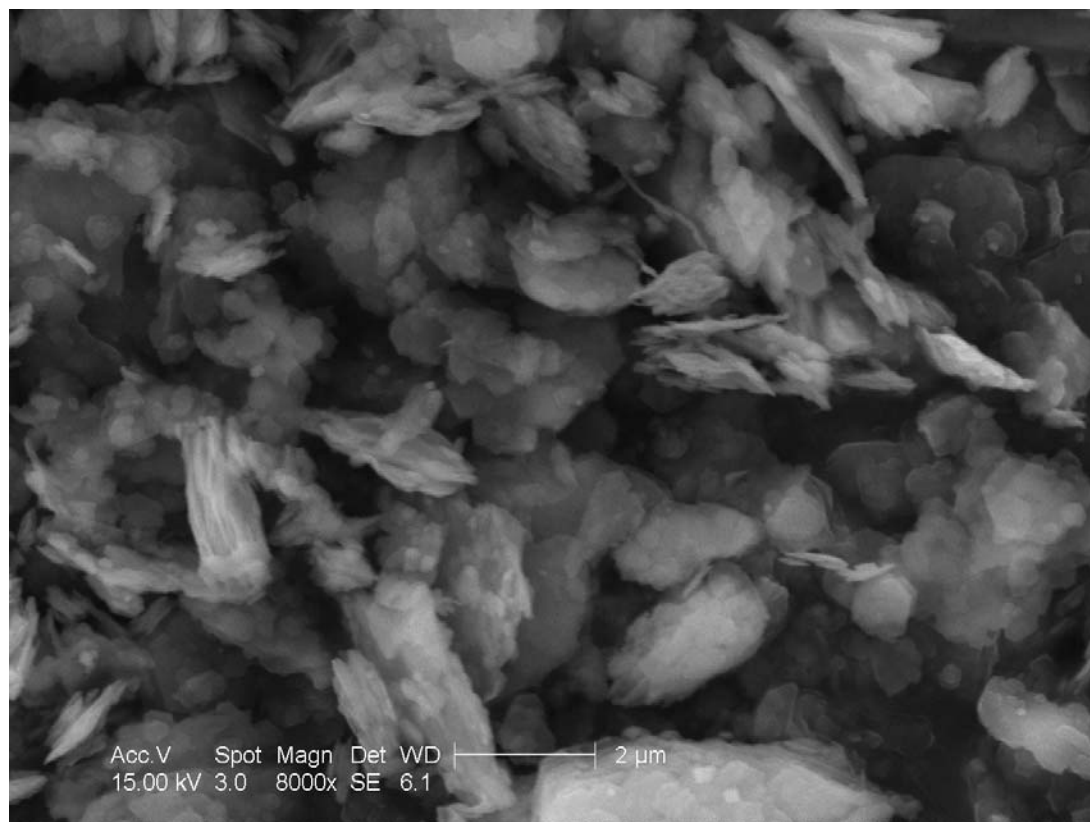


Figure 32. SEM of filter cake from condition 4, from dark area on filter.

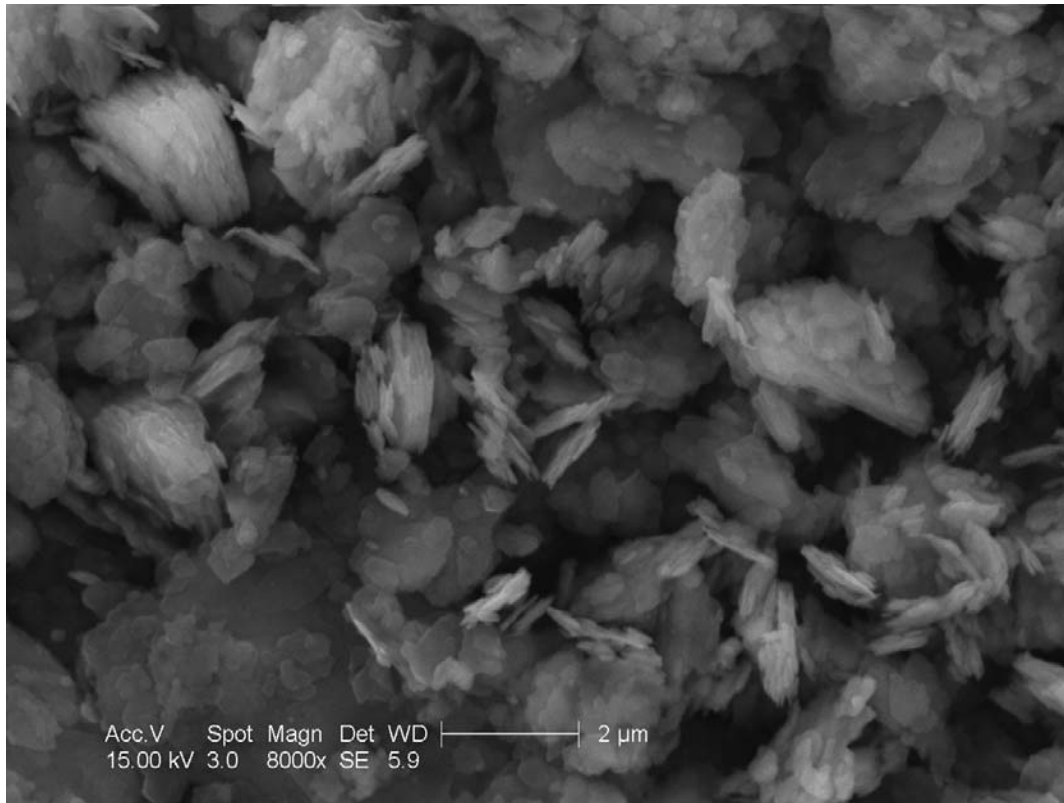


Figure 33. SEM of filter cake from condition 4, from light area on filter.

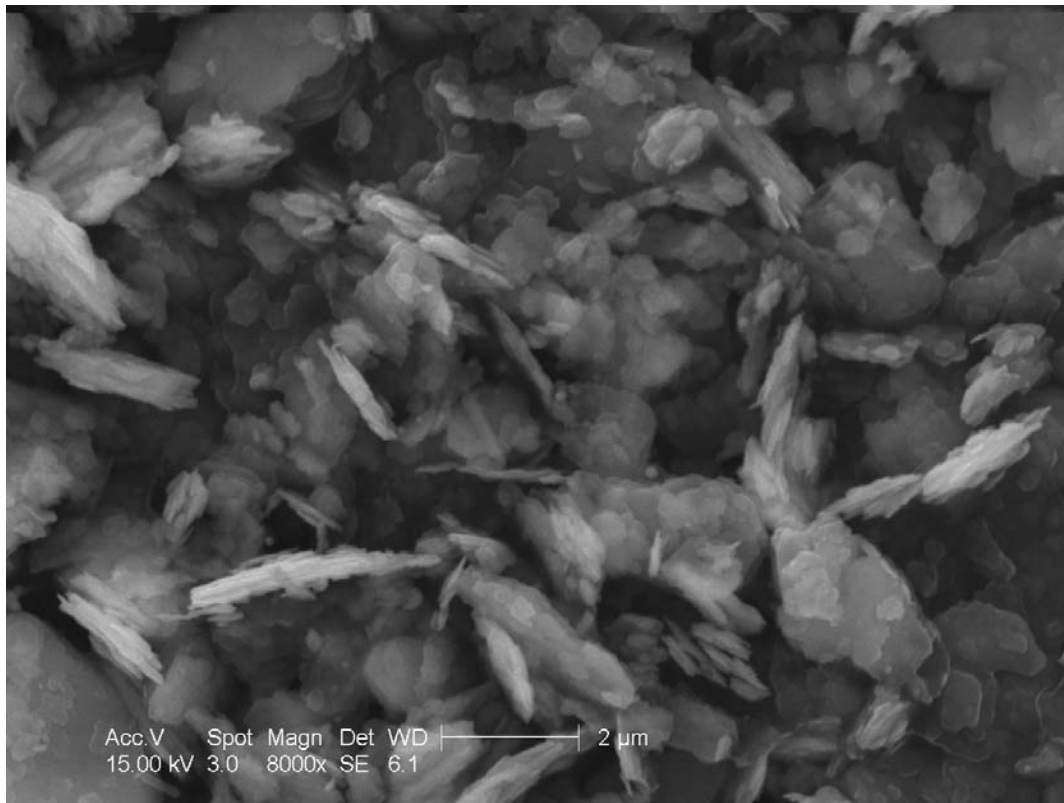


Figure 34. SEM of filter cake from condition 5, from dark area on filter.

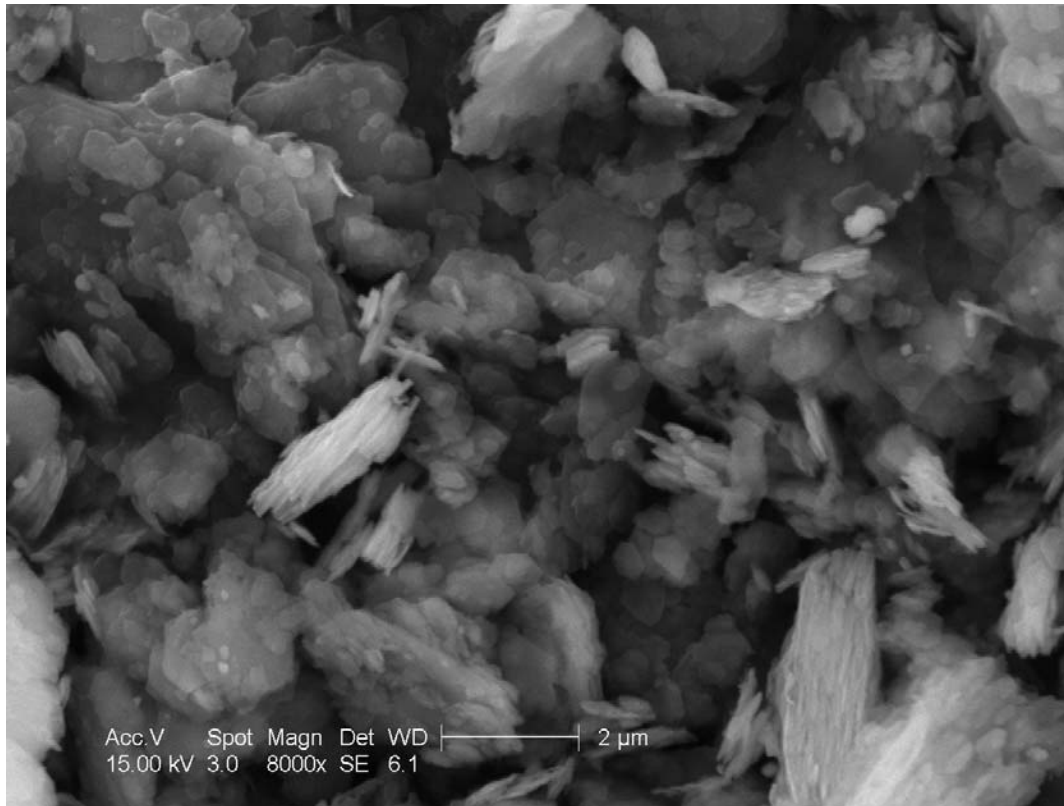


Figure 35. SEM of filter cake from condition 5, from light area on filter.

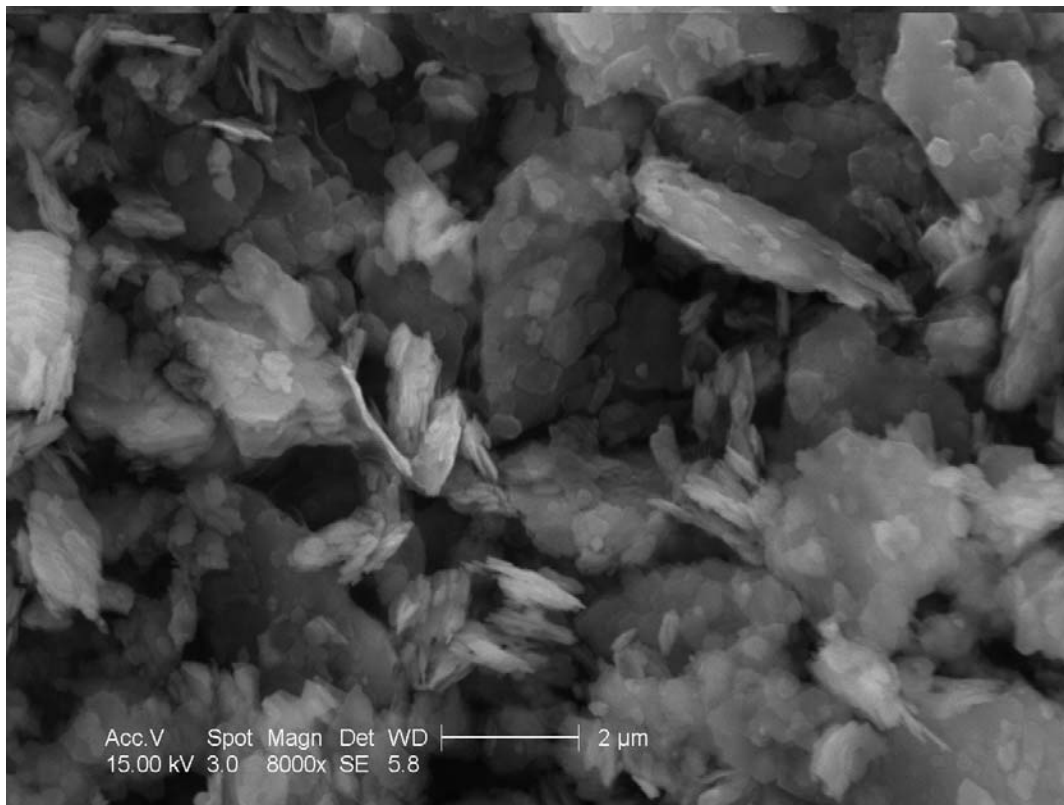


Figure 36. SEM of filter cake from condition 6, from dark area on filter.

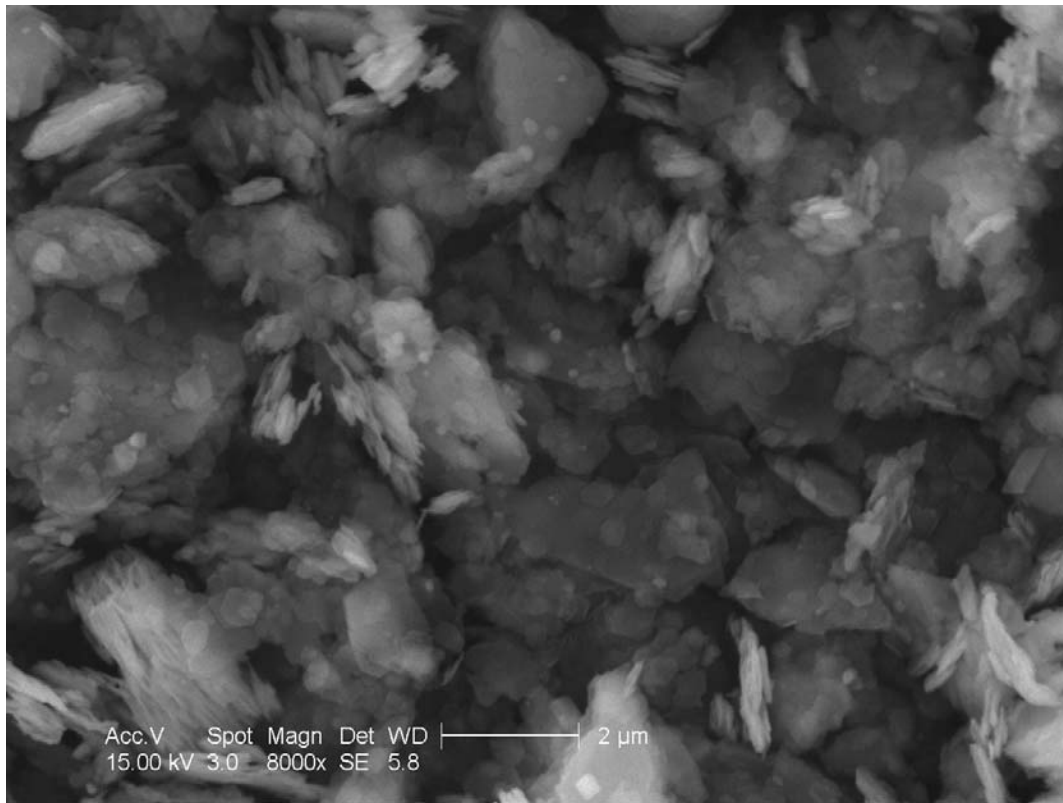


Figure 37. SEM of filter cake from condition 6, from light area on filter.

Modeling

Working models have been developed to accurately describe the reactive capture of semi-volatile metals by powder sorbents. These models are metal and sorbent specific and include multi-metal interactions [1-3, 5]. These models are based on the mechanisms governing metal capture by dispersed powder sorbents in a temperature range between 1000 and 1300 °C, with residence times in the range of 0.84 to 1.15 seconds. Under these conditions, eutectic melting significantly effects metal capture by enhancing the sorbent utilization and capture rate for certain conditions and by deactivating the sorbent with a catastrophic sorbent melt (closing pores) under other conditions [1-3, 5]. These models are all global mechanistic models, fit to the data.

In an effort to develop more fundamental models, including many of the known gas-phase reactions, ChemKin [41], a chemical kinetics code containing hundreds of basic reactions and kinetic rates was used to assist. Work on this fundamental model has yielded a description of the gas-phase species of sodium and potassium and the major gas-phase reactions of these species in syngas [22, 42]. As expected, the gas-phase reactions are sufficiently fast to allow the gas-phase reaction products to follow equilibrium concentrations throughout the system. Figures 38 through 40 illustrate the change in potassium species as a function of temperature, for syngas derived respectively from corn stover, switch grass, and wheat straw, based on thermochemical equilibrium calculations [42], made using CEA, a thermochemical equilibrium program [34]. It is important to note that these thermochemical equilibrium predictions were made without including gas-solid reaction products.

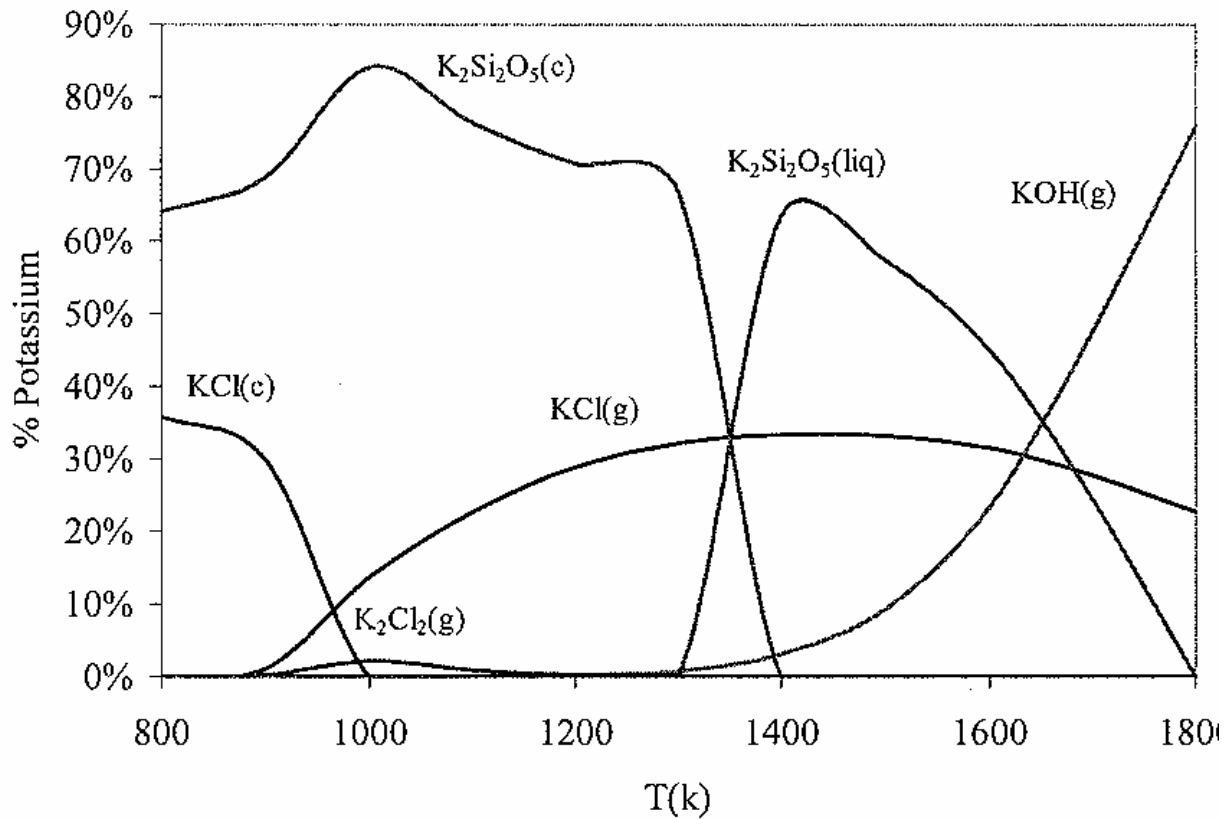


Figure 38. Speciation of potassium in syngas derived from corn stover [42].

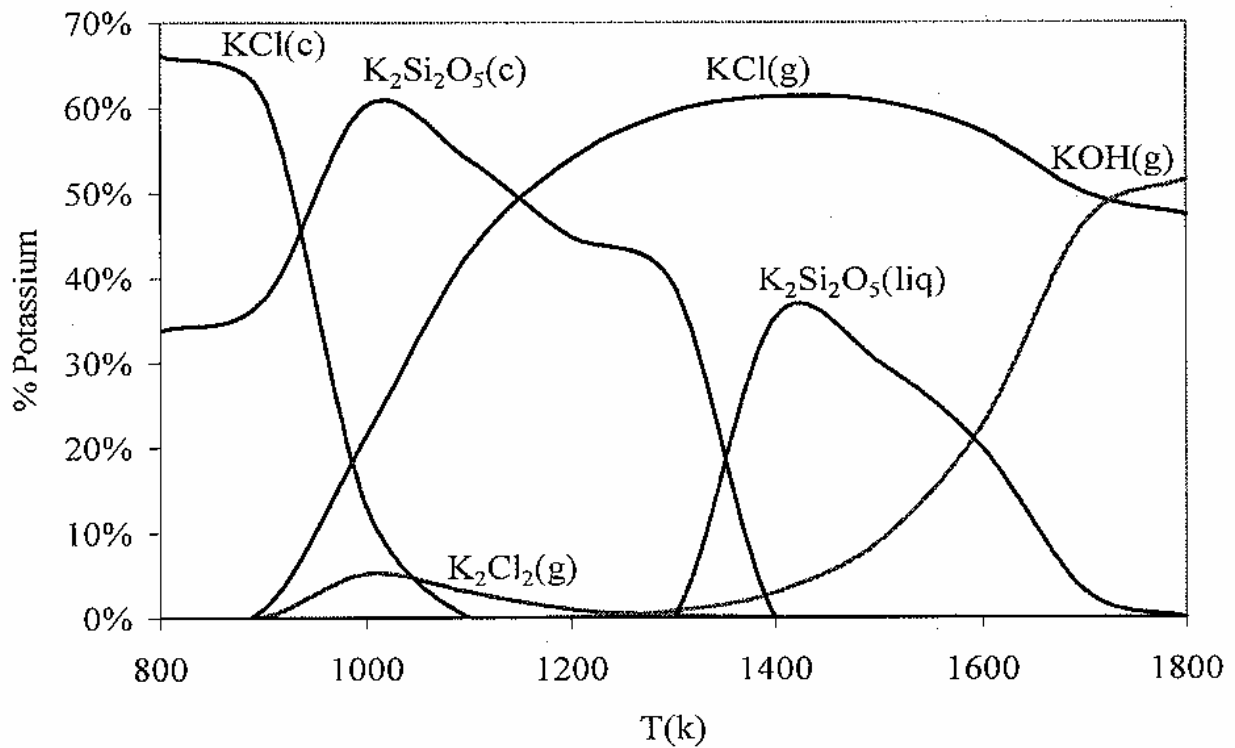


Figure 39. Speciation of potassium in syngas derived from switch grass [42].

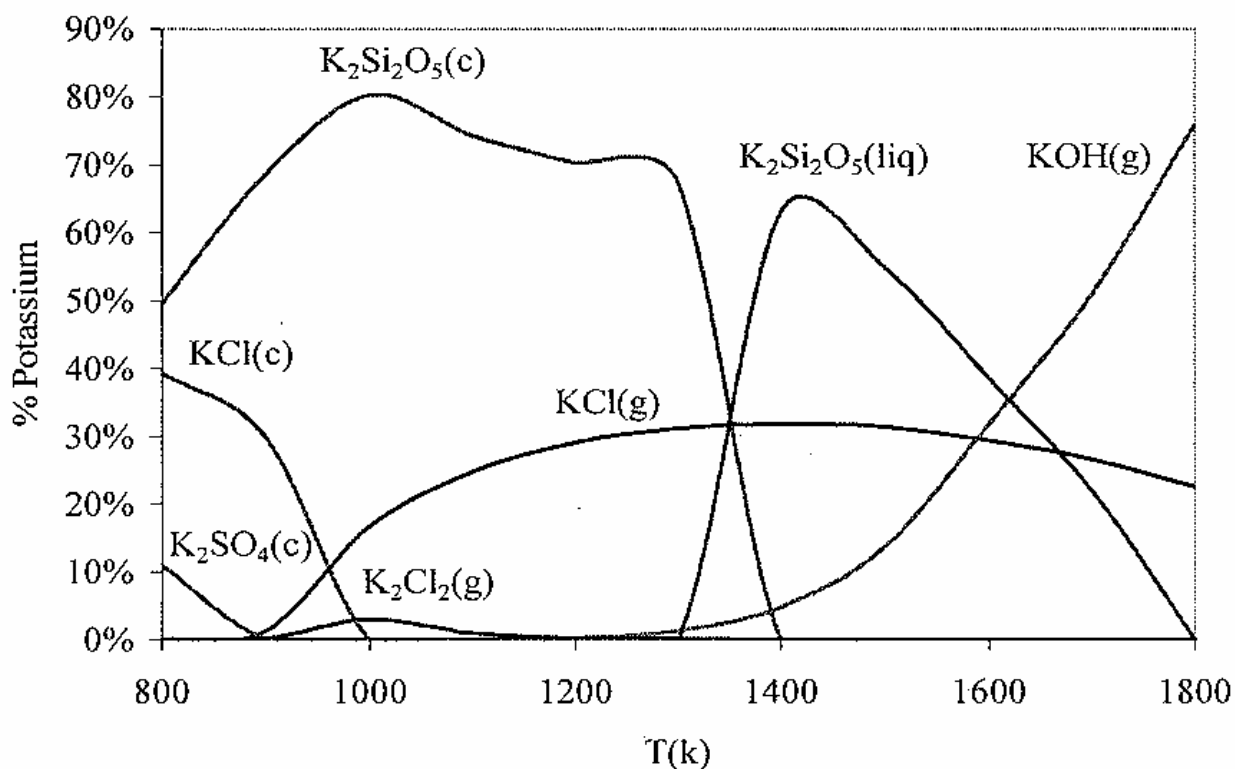


Figure 40. Speciation of potassium in syngas derived from wheat straw [42].

Figures 38-40 illustrate potassium speciation at atmospheric pressure, for three different syngas types. Figure 41 illustrates the effect of pressure on potassium speciation, for syngas derived from switchgrass. While pressure does have an effect, it is not dramatic in terms of determining the condensation temperature of potassium in syngas.

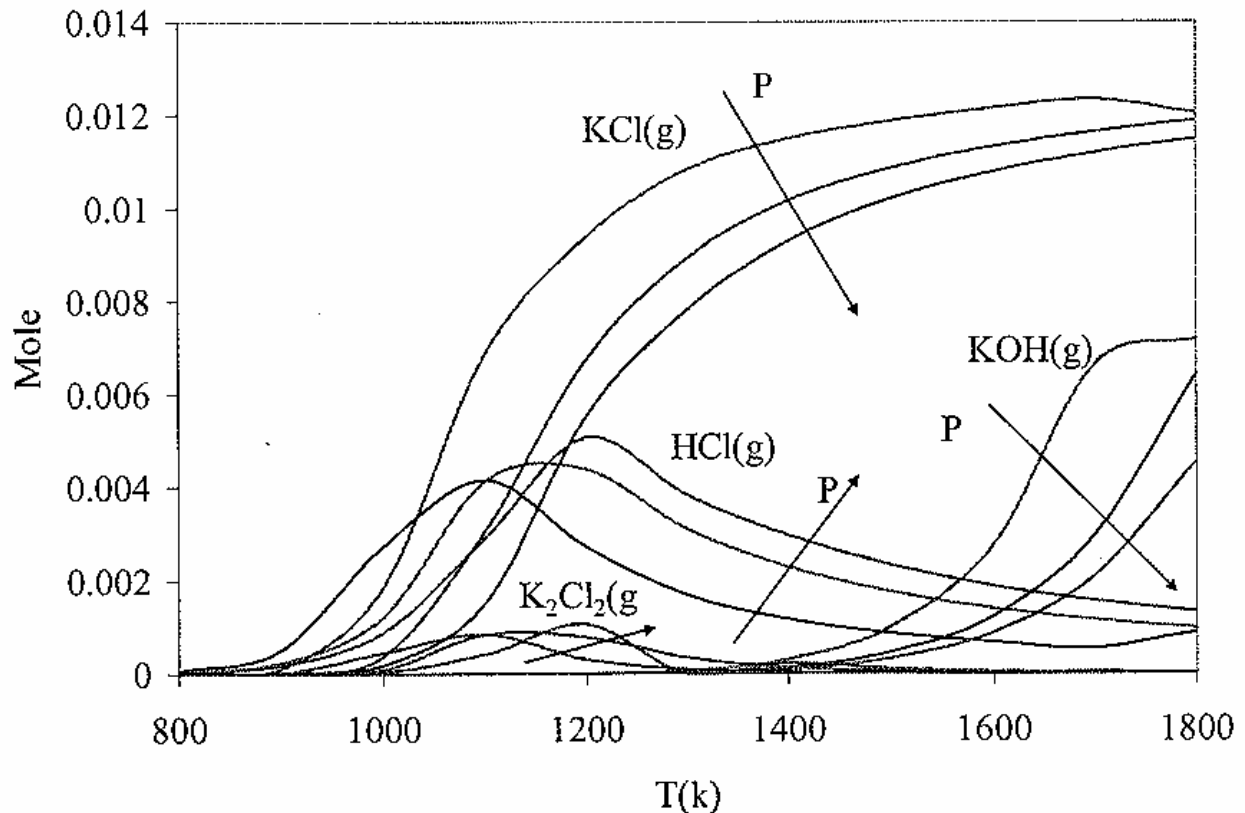


Figure 41. Effect of pressure (1, 5, and 10 atm) on potassium speciation in syngas derived from switchgrass [42].

As shown in Figures 38-41, the bulk of the potassium is predicted to condense by 1160 °F (900 K). Although this is a higher temperature than many syngas-cleanup systems are currently expected to operate at (i.e., ~800 °F is the operating temperature anticipated for many candle-filter systems), this is not a guarantee that all of the alkali metals will condense. The dew point of each metal is concentration dependent as well as temperature dependent, and trace amounts of metal vapor (particularly semi-volatile metal vapor) may be present in the syngas, even though the bulk of the metal has condensed. In addition, trace amounts of minor species heretofore less investigated (i.e., organic metal compounds) may also allow trace amounts of metal to penetrate the barrier filter at lower temperatures. Therefore, much lower temperatures are required to ensure that not even a small concentration of metal will be in the vapor-phase as it hits the barrier filter. Since even parts per trillion concentrations of alkali metals can damage turbine blades and syngas-reforming catalysts and similar concentrations of heavy metals can increase human health risks, there is still a need to develop technologies that can provide increased resistance of barrier filters to alkali- and toxic-metal penetration.

Work had begun to expand the chemical kinetics model to include metal/sorbent capture mechanisms, which add significant complication to the model, but which would endow the model with the ability to actually predict the mechanisms, transformations, metal capture, and effects on the filter that occur in the syngas cleanup system. Eventually, it was intended to develop a model that could completely describe all aspects of syngas speciation, including tar

formation and destruction, COS, H₂S, and NH₃ formation, destruction, and/or capture, metal speciation and capture, ash/char transformation, sorbent transformations, and candle-filter damage and protection. Unfortunately, the funding was cut on this project at a critical time of the development of this model, such that the modeling work halted at the beginning of this step.

CONCLUSIONS

A small reactor was designed, built, and successfully operated, which effectively mimics the hot-syngas process environment. As would be the case with high-temperature sorbent technology in a full-scale system, (a) the reactor allows sorbent injection into the syngas (actual or simulated) at a temperature representative of the syngas between the gasifier and the PCD (i.e., between 1500 °F and 800 °F), (b) the reactor allows dispersed sorbent/syngas residence times of fractions of a second to several seconds before the sorbent is collected on the filter as the syngas passes through it, and (c) the reactor maintains the candle filter element (i.e., same candle material as used in the demonstration unit) at the full-scale operating temperature (e.g., ~800 °F) and allows the sorbent to collect on this filter and build up as it would in a full-scale system. This reactor also allows doping of trace or primary metals into the syngas stream, in order to study the effect of specific metal concentrations.

A major initial objective of the project was accomplished, which was to determine whether or not high-temperature sorbents found to work within vitiated air might also work in an inert environment. Kaolinite, one of the sorbents previously investigated as a high-temperature sorbent for incinerators, was found to effectively capture potassium, in an inert environment. In addition, while previous work on short-time (i.e., 1 to 2 seconds) dispersed-phase reactions found that sorbent utilization was limited to two metal oxide species captured for every one aluminosilicate crystal structure, the present investigation found that many times higher insoluble metal/sorbent capture ratios were obtained. This result not only suggests that small additions of sorbent might be highly effective, but the fact that the products were insoluble (in part due to the temperature of sorbent injection, i.e., < 1500 °F) may be an indication that the products are unlikely to react with, corrode, or otherwise damage the candle-filter elements. The findings not only validate kaolinite as a high-temperature sorbent in an inert environment, they also show that potassium can be effectively captured by these sorbents, which there had been very little data available on previously, even for capture from incinerator or combustion flue gases.

REMAINING WORK TO BE ACCOMPLISHED

An initial goal for this work was to establish the effectiveness of high-temperature sorbents in inert and syngas environments, for use in cleaning biomass-derived syngas prior to use in producing liquid fuels and chemicals. The first part of this goal was established, as stated in the conclusions. That is, kaolinite powder, with a crystalline structure indicative of an important class of high-temperature sorbents, was effective at scavenging potassium from an inert environment and forming insoluble (presumably sequestered and benign) products. These results are very promising for this technology potential, along with the results indicating that the sorbent utilization was extremely high under the actual operating conditions for this technology implementation.

Unfortunately, Congressional budget cuts early on in the course of this project significantly hindered the progress of this work, and now the project must halt while still having very important questions to answer.

Following is an explanation of that which still needs to be done on this project and the questions that will be answered, if this project is funded and allowed to proceed in the future.

Kaolinite has now been shown to effectively capture metals in an inert environment, and to do so at temperatures consistent with hot-gas cleanup systems and candle filters. The effects of a reducing environment on kaolinite and other sorbents still needs to be evaluated. Subsequently, the effects of real syngas on these sorbents also needs to be evaluated and quantified, including the impact of multiple metals, tars, and acid gases.

Kaolinite was found to effectively capture potassium from an inert environment at relatively high temperatures, which was a newly discovered fact that has significant relevance to hot-gas cleanup of biomass derived syngas.

While potassium scavenging is of great interest relative to cleanup of biomass-derived syngas, the potential of high-temperature sorbents to scavenge other metals, such as Na, Pb, Cd, Se, As, Ni, and Cr, is also very important and has yet to be fully investigated.

Other sorbents besides kaolinite, such as calcium-based sorbents and waste-derived sorbents, need to be tested as well. Each of these sorbents needs to be tested in inert, reducing, and real syngas environments. In addition, the effectiveness of each of these sorbents at capturing different metals from syngas and combinations of metals needs to be evaluated, and quantitative correlations and models should be derived therefrom. Ultimately, inexpensive waste-derived sorbents should be developed based on this information that will optimize the capture of the metals and protection of the barrier filters for each individual application.

This project has focused on one filter element so far, the iron aluminide filter, because it was being used at the PSDF at the time. However, different candle-filter types should be used in these evaluations in the future, to determine the relationship between syngas composition, sorbent type, and the type of candle-filter element used.

The effect of different temperatures and pressures on the effectiveness of sorbent at capturing metal and protecting the filters also needs to be evaluated.

The impact of tars on sorbents and sorbents on tars also needs to be considered, and is one of the major questions about this technology.

In order to properly investigated the parameters listed above and evaluate the effectiveness of the technology, additional measurements will need to be made, many of them quite difficult. It will be important to find a method of measuring the trace amount of metal vapor that escapes through the candle filter, during each test condition, which metal concentrations may only be in the parts per trillion range. Nevertheless, these trace emissions can damage the blades of a gas turbine and

hinder the processing of the syngas into liquid chemicals and fuels, by damaging reforming catalysts or otherwise.

Finally, after the bench-scale and slipstream testing is complete, it will be necessary to have a larger-scale demonstration of this technology, to determine the full-scale type impacts this technology will have.

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