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SELENIUM EMISSION CONTROL AT HIGH TEMPERATURES WITH MINERAL SORBENTS

Final Report for the Period
September 1, 1994 to February 29, 1996

by

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EXECUTIVE SUMMARY

The Focus of this project is on toxic heavy metal removal by sorbent injection in the upper furnace and economizer sections of a coal-fired boiler. Selenium was chosen as the candidate heavy metal to be studied because of its high volatility and associated difficulties in removal. Mercury being the most volatile of all the trace elements present in coal, has already being singled out for extensive studies by different research programs, funded by EPA, DOE, and EPRI. However the results of the proposed study can be suitably extended to tackle emission problems related to other trace heavy elements. SeOV ?

A thorough mechanistic investigation of the Se-$Ca(OH)_2$ interaction at both medium and high temperatures has been conducted in this project and is published as a paper entitled, "Selenium Capture using Sorbent Powders: Mechanism of Sorption with Hydrated Lime," to the *Environmental Science & Technology* journal. Experiments were performed in the two temperature ranges in the presence and absence of O_2; desorption studies were conducted to characterize the nature of interaction; and XRD/XPS and Ion Chromatography studies were performed for species identification. It was inferred from these findings that the selenium capture was significantly more in the medium temperature range (450-650°C) than in high temperature range (800-1000°C) and the captured selenium species in the medium temperature range is in the form of calcium selenite ($CaSeO_3$) and a reaction scheme was proposed for the CaO/SeO_2 interaction:

$$CaO\,(s) + SeO_2\,(g) = CaSeO_3\,(s)$$

This reaction process does not require the participation of oxygen, as was confirmed by various analytical techniques and supported by the experimental evidence.

Results of the high-temperature studies indicate much reduced capture at these temperatures with negligible selenium sorption above 900°C. In contrast to the medium-temperature runs, results at these temperatures show a decreasing selenium capture by the sorbent as temperature increases. This behavior was attributed to the decomposition of calcium selenite at higher temperatures.

An Entrained Flow Reactor (EFR) system was designed and constructed in order to study the short time Se-$Ca(OH)_2$ interaction under entrained flow conditions. the EFR system was designed to conduct experiments with residence time in the range of 1-5 seconds and at temperatures upto 1000°C. Experiments were conducted in the EFR to test the capturability of selenium species by $Ca(OH)_2$. Results from these experiments indicate that $Ca(OH)_2$ captured as much as 1100 ppm of selenium species for a residence time of 3.0 seconds under entrained conditions. Thus suggesting the feasibility of Dry Sorbent Injection technique in removing selenium species from flue gas by using calcium based sorbents.

In actual flue gas atmosphere Ca-based sorbents are exposed to various gaseous species including SO_2. The presence of SO_2 along with SeO_2, in the gas phase, could lead to various interactions. Experiments were conducted to determine the selenium capture by the $Ca(OH)_2$ sorbent, under differential conditions, in an atmosphere with containing SO_2. Results from these experiments indicate that $Ca(OH)_2$ interacts independently with SO_2 and SeO_2 (no significant gas phase interaction between SeO_2 and SO_2 in the temperature window of interest) in medium temperature range forming $CaSO_4$ and $CaSeO_3$ respectively.

I. OVERVIEW

A. Background and Scope:

The focus of this project is on heavy metal removal by mineral sorbent injection in the upper-furnace region (800°-1100°C) and economizer section (450-650°C) of a coal fired boiler. Selenium is chosen as the candidate heavy metal to be studied because of its high volatility and associated difficulty in removal. Selenium content of Ohio coals is substantially higher in comparison to national and world averages. The present technology is inadequate to meet the anticipated toxic emission standards, expected to be enforced by EPA in near future. As the regulations on toxic emissions from the coal-fired utility plants are getting stricter, idea of a single process capable of substantially reducing most of the toxic emissions sounds very appealing. Proposed study is the first step towards developing such a process.

A promising technique for removal of metal vapors from hot flue gases is by injecting sorbents into the gas stream. Although the work on high-temperature removal of heavy metals by sorbent is scarce, its appeal is great considering the relative success of various sorbent injection studies for the flue gas desulfurization. With this goal, the purpose of this project is to identify the most efficient sorbent available in removing Se and its compounds from the flue gas and to investigate the feasibility of furnace sorbent injection technique for the control of trace metal emission from coal fired combustors.

Mechanistic understanding of Se/sorbent interaction is essential to determine the various parameters which influence this interaction. This knowledge would ultimately lead to the development of a better and more efficient sorbent. A portion of second year of the project was devoted to complete the study of the sorbent-Se interaction, which was started in the later half of the first year, in the differential bed reactor system to get a further insight into the capturing mechanism. Results from interaction studies suggest that the Se-$Ca(OH)_2$ interaction is chemical in nature and capture of selenium species takes place via a chemical reaction resulting in the formation of $CaSeO_3$. Presence of calcium selenite was confirmed by XRD and XPS analyses of the post sorption sorbent sample. Furthermore it was also determined that the most favorable temperature window for selenium capture is the medium temperature window with maximum capture shown at 600°C under the given experimental conditions.

As proposed, significant part of the second year was spent on designing and developing an Entrained Flow Reactor (EFR) system to study the capture of selenium species by $Ca(OH)_2$ under entrained conditions. Development of EFR system was carried out in conjunction with project 4.2. Experimental studies were carried out in the EFR system and the results from these studies indicate that in the medium temperature range of 450°C to 600°C removal of selenium species from the flue gas was significant.

B. Long Term Objectives:

The long term objective of this research project is to deliver the following:

1. identify those mineral sorbents which show most promise in capturing selenium.
2. investigate the mechanism of Se capture by the sorbents.
3. if any, identify the chemical compound formed by Se/sorbent interaction
4. determine the feasibility of injection technique in Se removal from flue gas by conducting short contact time studies in an entrained flow reactor within the applicable temperature window.

II. DIFFERENTIAL BED REACTOR STUDIES: CAPTURING MECHANISM

A. Differential Bed Reactor Studies:

Sorption studies were carried out in the differential bed reactor system developed in the first year of the project. Figure 1 shows the results of the sorption studies in terms of overall capture at different temperatures in the medium and high temperature ranges. The overall sorption is seen to increase with temperature between 400 to 600°C, however, it reduces drastically at higher temperatures yielding a maxima at 600°C. Figure 2 compares the selenium capture by $Ca(OH)_2$ in the presence of air with that under inert nitrogen at medium temperature conditions. The amount of sorption under diluent air is observed to be less than that under nitrogen and the difference is more pronounced at the lower temperatures of 400 and 500°C. Carbonation of CaO to $CaCO_3$ due to the presence of CO_2 in air appears to be the most probable reason for reduced metal capture under air. Carbonation of CaO ~~is known~~ to be a competitive reaction in this temperature range from related work on Ca/SO_2 reaction at medium temperatures [1]. This is verified by heating a small amount of the post-reaction sorbent in a TGA immediately after withdrawal from the reactor. The TGA result indicates that significant portion (30-50%) of the sample CaO is carbonated to $CaCO_3$ during the sorption run. Carbonation occurs preferentially on and near the CaO surface, and $CaCO_3$ being highly non-porous may block SeO_2 access to the interior oxide surface. This phenomenon in association with loss of overall CaO can be used to explain the reduction in metal capture observed for 400 and 500°C runs. At 600°C and higher temperatures, carbonation of CaO is not very significant and the results are nearly identical for both nitrogen and air.

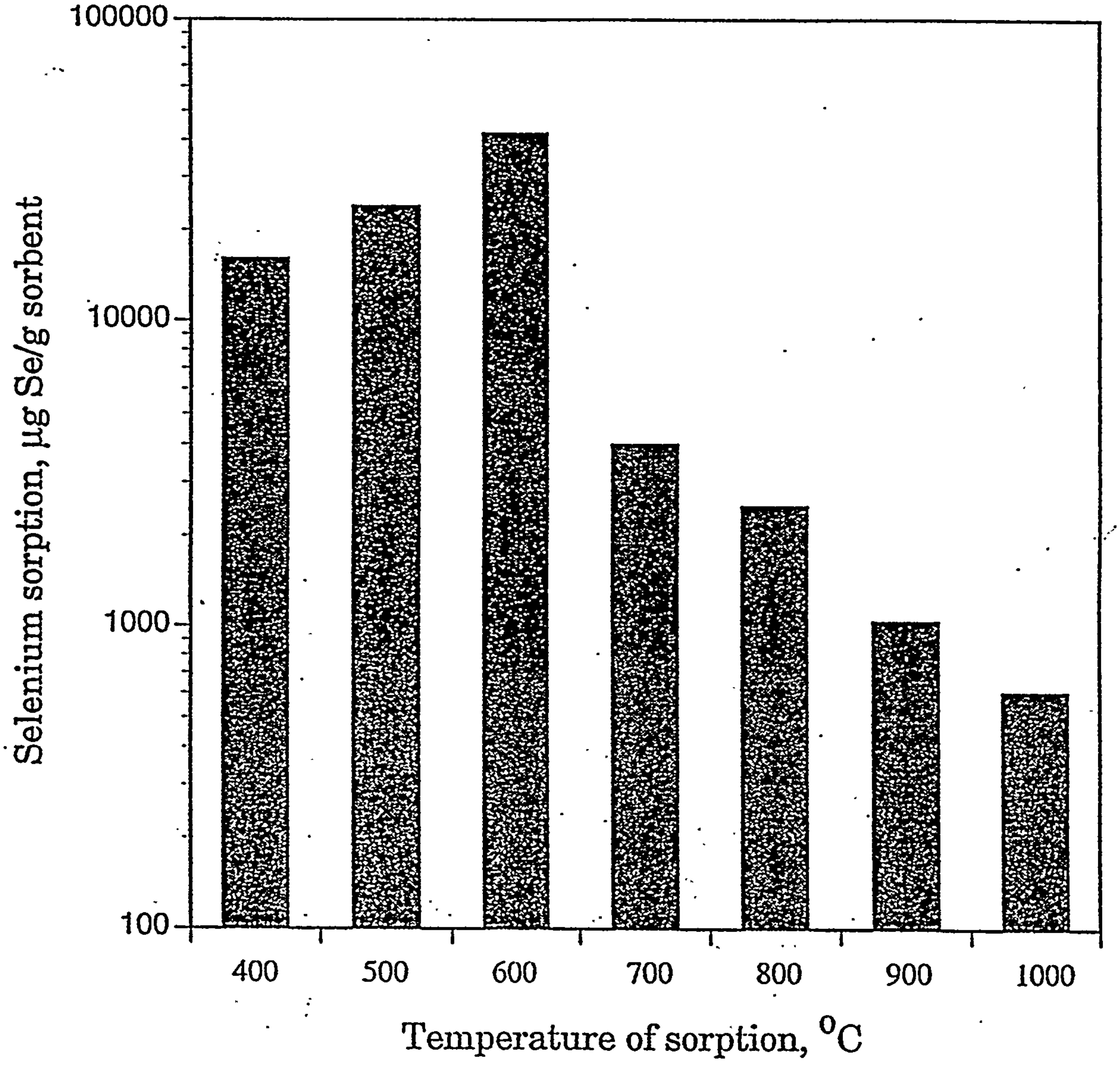


Figure 1: Selenium uptake by $Ca(OH)_2$ sorbent in 4 hours; selenium concentration: 8 ppm; diluent stream: air.

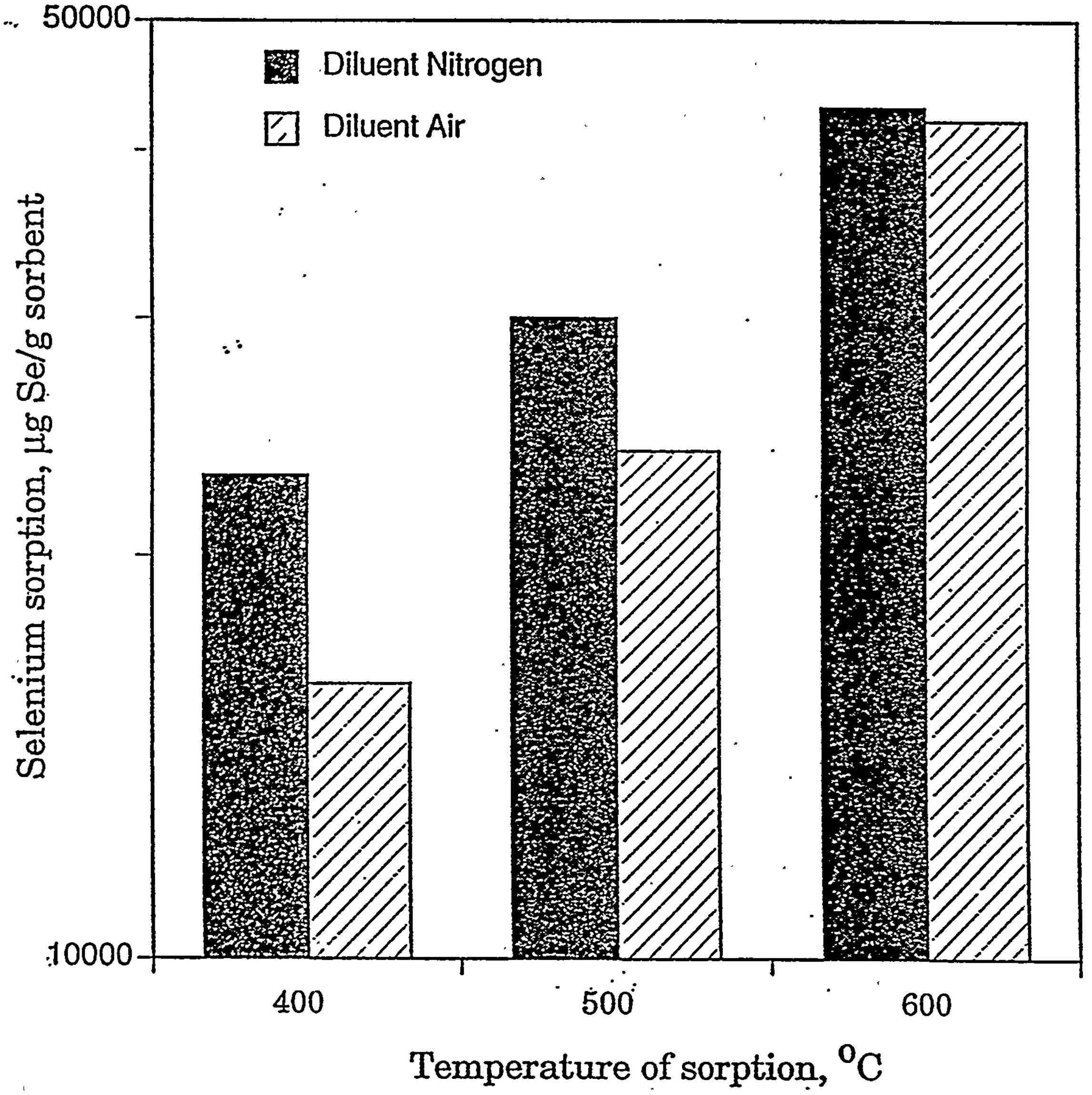


Figure 2: Comparison of selenium capture by $Ca(OH)_2$ sorbent under different diluent streams; ■ Nitrogen, ▨ Air; concentration of Se: 8 ppm

B. Capturing Mechanism:

The actual mechanism of Se sorption by CaO could involve either physisorption of SeO_2 or some chemisorbed complex or some chemical reaction product from CaO and SeO_2 (to yield a calcium-selenium-oxygen compound such as $CaSeO_4$ or $CaSeO_3$) or a combination of all these phenomena. Physical adsorption involves relatively weak attractive forces between the adsorbent and adsorbate, and the physisorbed amount decreases rapidly with increasing temperature [2,3]. Further, physisorption is a nonactivated process and easily reversible. As a result, an increase in temperature or a decrease in gas phase concentration of the adsorbate species decreases the equilibrium amount of the physisorbed species.

Water-leachability tests indicate that practically all the selenium captured at medium temperatures is in the water soluble form. SeO_2 is highly water soluble, as well as $CaSeO_4$ and $CaSeO_3$; hence water-leachability characteristics alone cannot distinguish between capture by physical adsorption and chemical reaction process. Analysis of the water leached solution of the 600°C sample using Alltech ion chromotography (IC) system showed the selenium to be present entirely in the form of selenite (SeO_3^{2-}) ion indicating a valence state of +4 for the selenium. This result demonstrates that Se content of the sample is present as either SeO_2 or calcium selenite, but not as more oxidized form of $CaSeO_4$ in which the valence state of the metal is +6. No appreciable difference in selenium capture between air and nitrogen environments at 600°C also suggests to an insignificant role of oxygen in the overall reaction process. The IC analysis also quantitatively corroborated the selenium concentration results obtained from AAS.

Desorption studies were carried out with the post-sorption sample by passing SeO_2-free nitrogen gas at the same flow rate at a specific temperature. Figure 3 shows the result of such isothermal desorption for the sorbent following sorption at 500°C. Negligible loss of selenium is observed following 2 hours of desorption at the temperature of sorption, i.e., at 500°C. Further desorption of the sample for 2 hours at higher temperatures of upto 700°C did not lead to any appreciable loss of selenium content. However, most of the selenium is released upon desorption at a much higher temperature of 825°C. The 400°C and 600°C samples also showed similar results following desorption for 2 hours at the respective sorption

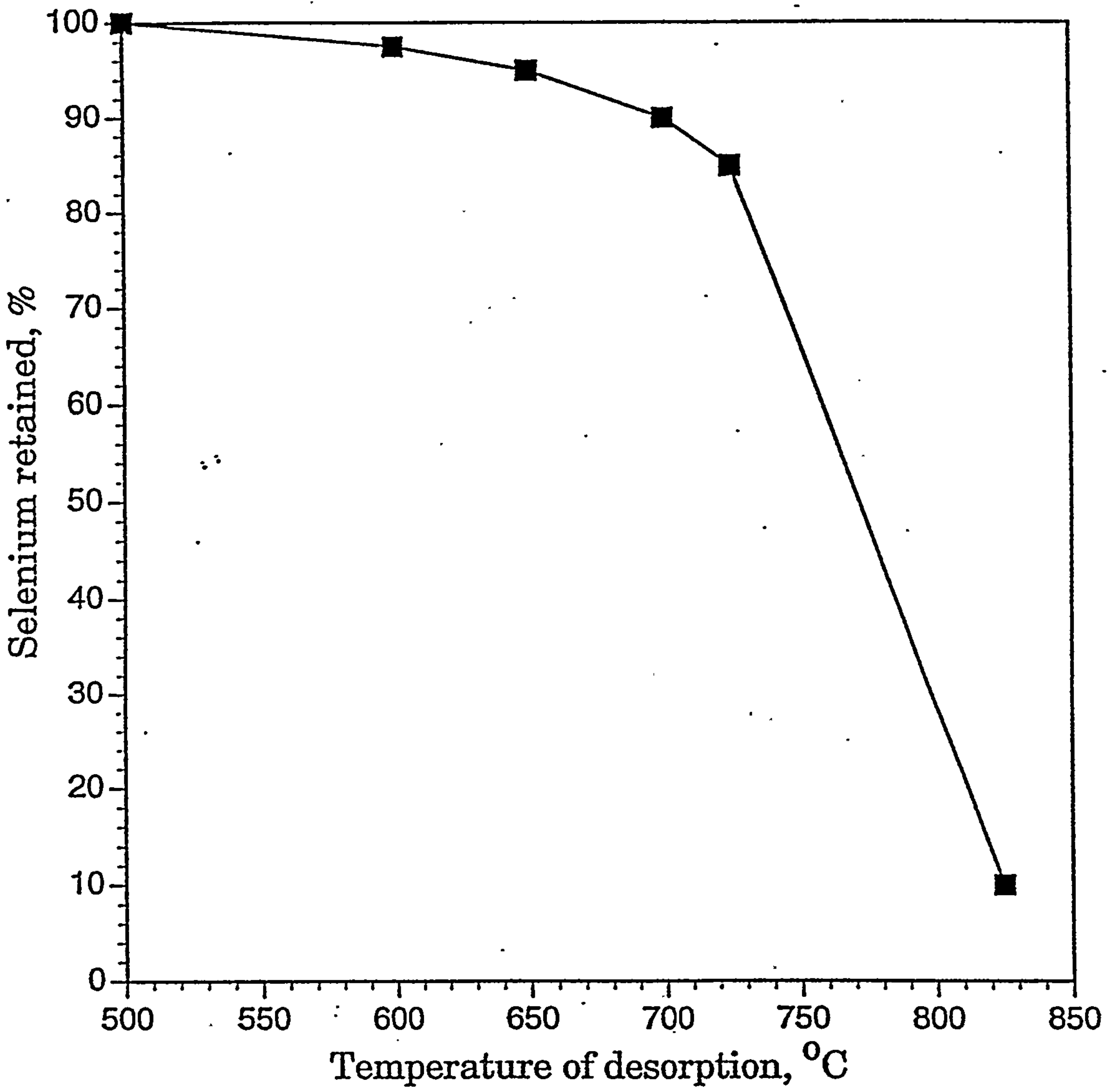


Figure 3: Effect of desorption temperature on selenium retention by $Ca(OH)_2$ sorbent following 2 hours of desorption under Se-free flow.

temperatures, which possibly indicate an irreversible capture of selenium, thus eliminating physical adsorption as a dominant mechanism in the sorption process.

In order to gain further insights into the actual mechanism of Se/sorbent interaction, sorption experiments are conducted for much longer time scale, and XRD/XPS are performed on the sorbent. Figure 4 shows the XRD spectrum of the sorbent following 48 hours of sorption at 500°C and at the same selenium concentration of 8 ppmv. From AAS analysis, the selenium sorption is about 150,000 μg Se/g sorbent. XRD spectrums are also performed for pure $CaSeO_4$ and $CaSeO_3$, in addition to SeO_2. Pure calcium selenate is procured from commercial sources as hydrated salts ($CaSeO_4.2H_2O$), and calcium selenite is prepared by decomposition of calcium selenate in the TGA at 700-800°C [4]. XRD seems to confirm the formation of calcium selenite on the sorbent from a comparison of these spectrums. On the other hand, the presence of physically adsorbed SeO_2 could not be confirmed by XRD. XPS results (Fig. 5a and 5b) also verified presence of selenium species on the sorbent surface, and a comparison of the sample spectrum with the $CaSeO_3$ and $CaSeO_4$ spectrums indicated that $CaSeO_3$ is the most likely chemical state of the captured selenium. Based on these findings, the following reaction scheme can be proposed for CaO/SeO_2 interaction:

$$CaO\,(s) + SeO_2\,(g) \leftrightarrow CaSeO_3\,(s) \qquad \text{(i)}$$

This reaction process does not require the participation of oxygen, which is further corroborated by XPS analysis on 600°C sample, reacted under air, which indicates presence of only $CaSeO_3$, but no $CaSeO_4$. Confirmatory tests are also performed in a TGA to study the stability of pure $CaSeO_3$ in the presence of oxygen at 600°C. Negligible weight gain following overnight exposure proves that $CaSeO_3$ does not react with oxygen to form selenate.

Results of the high-temperature studies indicate much reduced capture at these temperatures with negligible selenium sorption above 900°C. In contrast to the medium-temperature runs, results at these temperatures show a decreasing selenium capture by the sorbent as temperature increases. Investigations of decomposition of pure $CaSeO_3$ with temperature were performed under inert nitrogen flow. Unlike the sulfur salts of calcium for which vapor pressure and decomposition characteristics have been thoroughly investigated [5], no such information is available for the selenium salts of calcium. $CaSeO_3$ is observed to

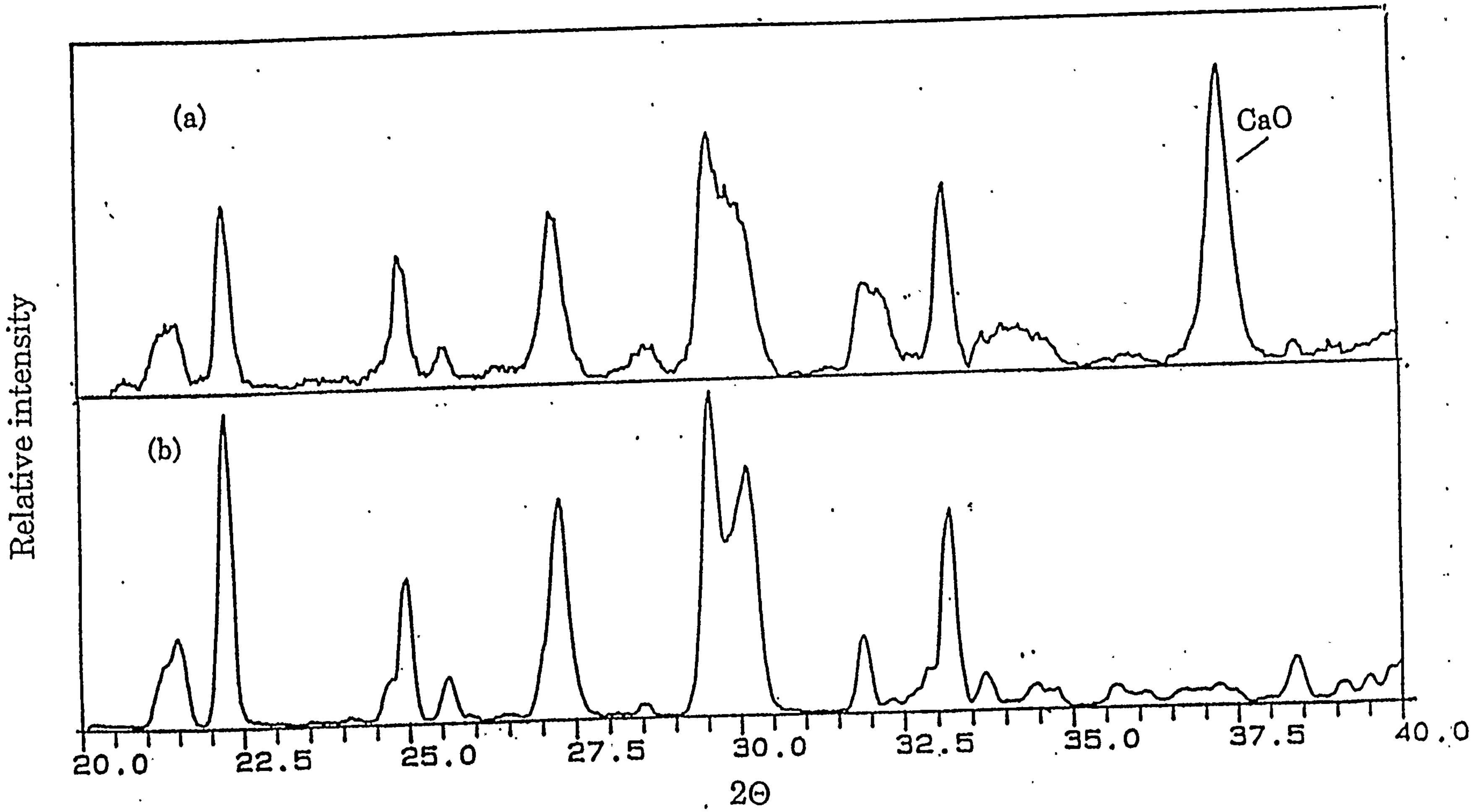
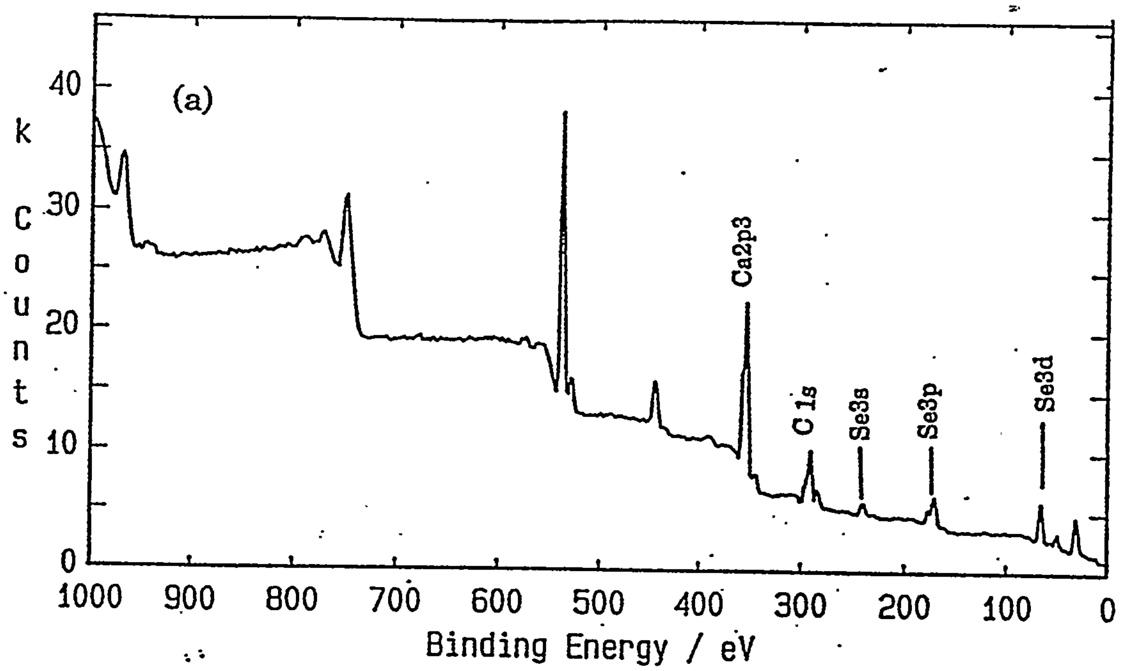


Figure 4: XRD spectrums of (a) post-sorption sample, and (b) pure calcium selenite; sorption conducted at 500°C for 48 hours under diluent air at selenium concentration of 8 ppm.



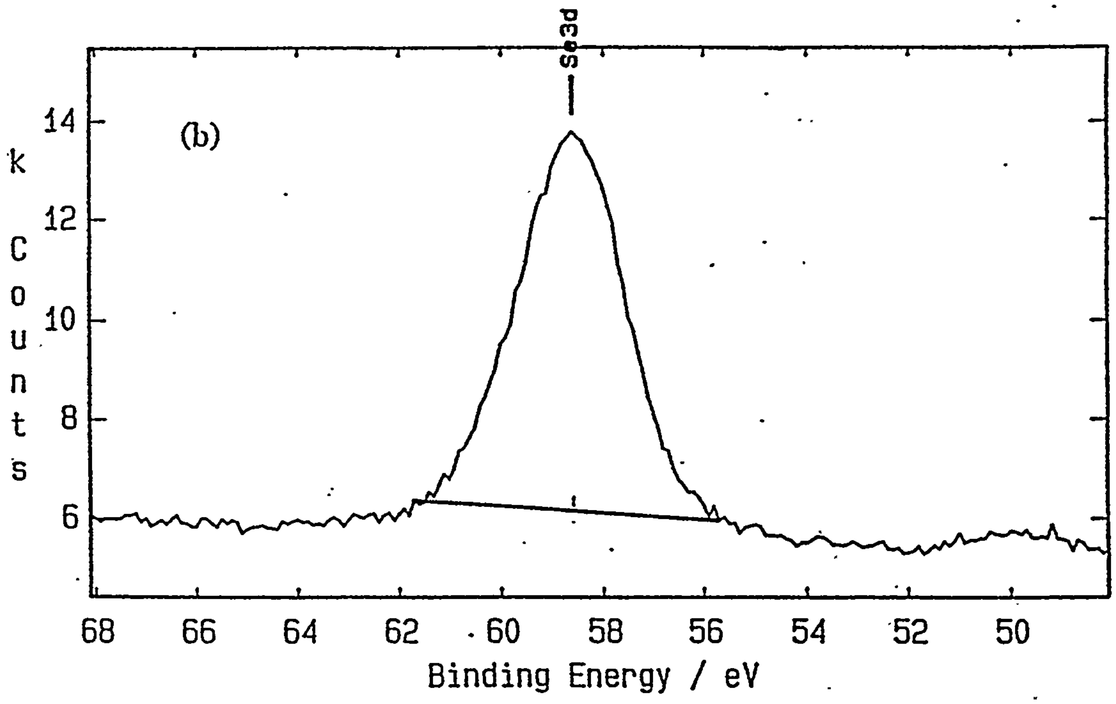


Figure 5: **XPS spectrums of (a) post-sorption sample, and (b) selenium 3d peak; sorption conducted at 600°C for 48 hours under diluent air at selenium concentration of 8 ppm.**

undergo decomposition after 800°C with the rate of decomposition increasing with temperature. The weight loss upon completion of decomposition corresponds to the formation of CaO. This indicates that in the reaction (i), the backward reaction becomes prominent at higher temperatures due to increasing vapor pressure of $CaSeO_3$. This is similar to the $Ca(OH)_2/SO_2$ reaction which shows an increasing rate of reaction upto about 1400 K and reduced sulfation at higher temperatures due to the decomposition of the reaction product $CaSO_4$ [6].

III. ENTRAINED FLOW REACTOR STUDIES

A. Entrained Flow Reactor:

An Entrained Flow Reactor (EFR) system was designed and developed in conjunction with project 4.2. A schematic diagram, shown in Figure 6, illustrates the main features of the this high-temperature EFR system. This rector system is capable of studying chemical reactions, in entrained conditions, with residence time in the range of 1-5 seconds and has a maximum operating temperature of 1000°C. The main component of the reactor system is a tubular reactor made out of Inconel 600 alloy. At the top, there is provision for mixing and entry of toxic-laden gas and sorbent powder. After traversing through the reactor section, the particle-gas mixture is quenched by dilution flow and the sorbent particles are separated from the gas using a cyclone and filter arrangement.

The main reactor consists of a 1.25" o.d. tube made of Inconel 600 and a wall thickness of 0.065”. The length of the reactor is 24”. Inconel 600 is superior to SS 316 for high temperature use and has the same ease of machinability, welding and fabrication [7]. The reactor tube will be housed inside a Thermcraft single-zone electric furnace. The furnace assembly is 18" in length and it will be placed vertically and has a split-hinge arrangement for ease of opening and closing. At the top of the reactor just above the furnace, there is a head section which has provision for entry of the reaction gases and sorbent. The top head section is fabricated separately from a SS 316 and is welded to the reactor tube. The bulk gas enters the reactor through the head section. The bulk gas tube is a 0.5" o.d. Inconel tube which is wrapped with heating tape in order to avoid condensation of vapor species. The bulk gas tube has provision for entry of the toxic-vapor laden gas and for the carrier gas transporting sorbent powder. The bulk gas consists of air (purged of CO_2) and is preheated by passing it through the furnace in a 1/8” o.d. SS 316 tube. Both powder and vapor enter the top section of the reactor at an angle of 45° to the bulk gas. Design of the top head section is such that it provides rapid heating and mixing of powder and vapor laden gases.

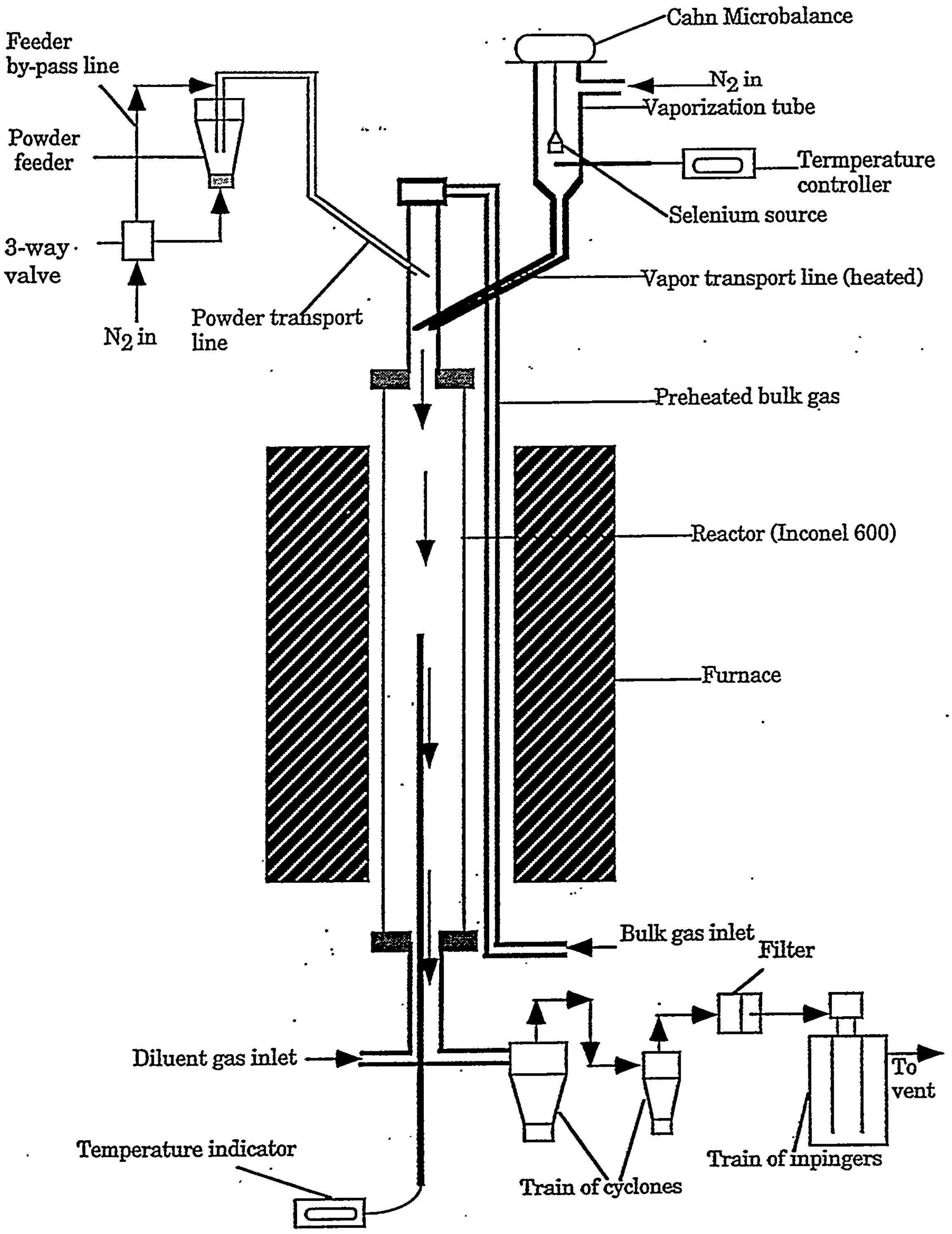


Figure 6: Schematic of Entrained Flow Reactor System for selenium sorption studies

The toxic vapor assembly is similar to the one being used for the fixed bed reactor assembly. It consists of the arsenic trioxide sample suspended from a microbalance assembly inside a quartz tube wrapped in heating tape. Temperature of the vaporization tube is monitored and controlled to maintain a steady SeO_2 vaporization rate. The bottom of the quartz tube is connected to a flexible stainless steel tube which serves to transport the toxic-laden gas. The entire flexible tubing line is also wrapped in heating tape and covered with insulation in order to prevent any condensation of the arsenic vapor. Toxic vapors thus generated, are carried away by a continuous flow of nitrogen gas through the vaporization tube. Vapor-laden nitrogen gas exits the vaporization tube from the bottom and is transported to the top section of the reactor by the flexible stainless steel tube. The whole vapor transport assembly is carefully monitored and maintained at temperatures above the vaporization tube temperature.

The sorbent powder feeder is a fluidized bed microfeeder similar to the one developed for Project 1.1. It consists of a sorbent powder bed fluidized by nitrogen gas and the entrained powder is transported through a 1/8" o.d. tube. The tip of the off-take tube is held just above the surface of the powder bed. The sorbent powder is fed into the reactor in a continuous manner. Powder feeding rate is kept very low to achieve proper dispersion and avoid clogging of the powder transport line. The powder enter lies above the vapor entry. This design feature is included to avoid vapor condensation in the powder line (a local cold spot) and to prevent reaction from occurring outside of the reactor.

Dry nitrogen will be used for the vapor transport as well as powder transport, while the bulk gas consists of air. The flow rate of the vapor-carrying gas will be about 200 ml/min. This is limited by the accuracy of the weight reading desired from the microbalance. The flow rate of nitrogen gas through the feeder is maintained at 800ml/min The powder carrier gas flow rate will be of the order of 0.5 lit/min, while the main bulk gas will be about 2.0 lit/min.

After traversing downwards through the reactor section, the gas-particle mixture exits from the bottom of the reactor. The gas-particle mixture flows out through a collection tube which is welded to the bottom head section. Bottom head is fabricated from SS 316 and is welded to the Inconel reactor tube. Before passing the gas-solid mixture through the phase separation unit the mixture is cooled to quenched the reaction. This is brought about by dilution of the hot reaction gases with cold purge nitrogen gas. Dilution of the reaction gases also reduce the concentration of the arsenic species in the gas phase thereby avoiding the excessive condensation of these vapor species. The saturation concentration of the arsenic trioxide is exponentially dependent on temperature. Cooling of the reaction gases to a temperature of about 200°C should be sufficiently low to prevent further reaction without causing condensation of the arsenic species in the line. Separation of solids from the gas stream is achieved by passing the suspension through a train of cyclones which are maintained at temperatures above the vaporization temperatures. Collected sorbent samples are analyzed for their captured arsenic content in an Atomic Absorption Spectrometer (AAS).

Residence time of the entrained species (sorbent particles) is calculated from the flow rate of the gases and the geometry of the reactor, after applying appropriate temperature corrections. The total flow rate of the gases was varied from 1.5 to 4.8 lpm (at STP) and the corresponding range of residence time was 1.25 to 4.0 seconds. Selenium vapor concentration was maintained at 8 ppm for all the residence times studied.

B. Results of Entrained Flow Reactor Studies:

Experiments were carried out to determine the extent of selenium capture by $Ca(OH)_2$ under entrained conditions. Experiments were conducted for three different residence times, viz, 1.25, 3.0 and 4.0 seconds. Results from the differential reactor studies have indicated that the most favorable temperature window for selenium capture by $Ca(OH)_2$ is the medium temperature window (400-600°C) with highest capture shown at 600°C. All the experiments in the EFR system were carried out at 600°C. To obtain different residence times the flow rate of the bulk gas was varied from 800 ml/min to 3800 ml/min. Table 1 gives flow rates of various gas streams and the amount of selenium dioxide vaporized (vapor phase concentration of selenium species at all the residence times was maintained at 8 ppm) for each residence time. All short contact time studies were carried out for a duration of one hour so that enough powder can be collected for post-sorption analyses. Figure 7, illustrates the amount of selenium captured at three different residence times at the reaction temperature of 600°C and

Residence time (sec)	Flow Rates (lpm at STP)			SeO_2 vap. (mg/hr)
	Bulk gas	Feeder N_2	Vap. N_2	
1.25	3.80	0.80	0.20	1.80
3.00	1.00	0.80	0.20	0.90
4.00	0.80	0.60	0.10	0.60

Table 1: Flow rates of different gas streams and amount of SeO_2 vaporized at various residence times (overall selenium vapor phase concentration is kept constant at 8 ppm at all times)
Reaction Temperature : 600°C

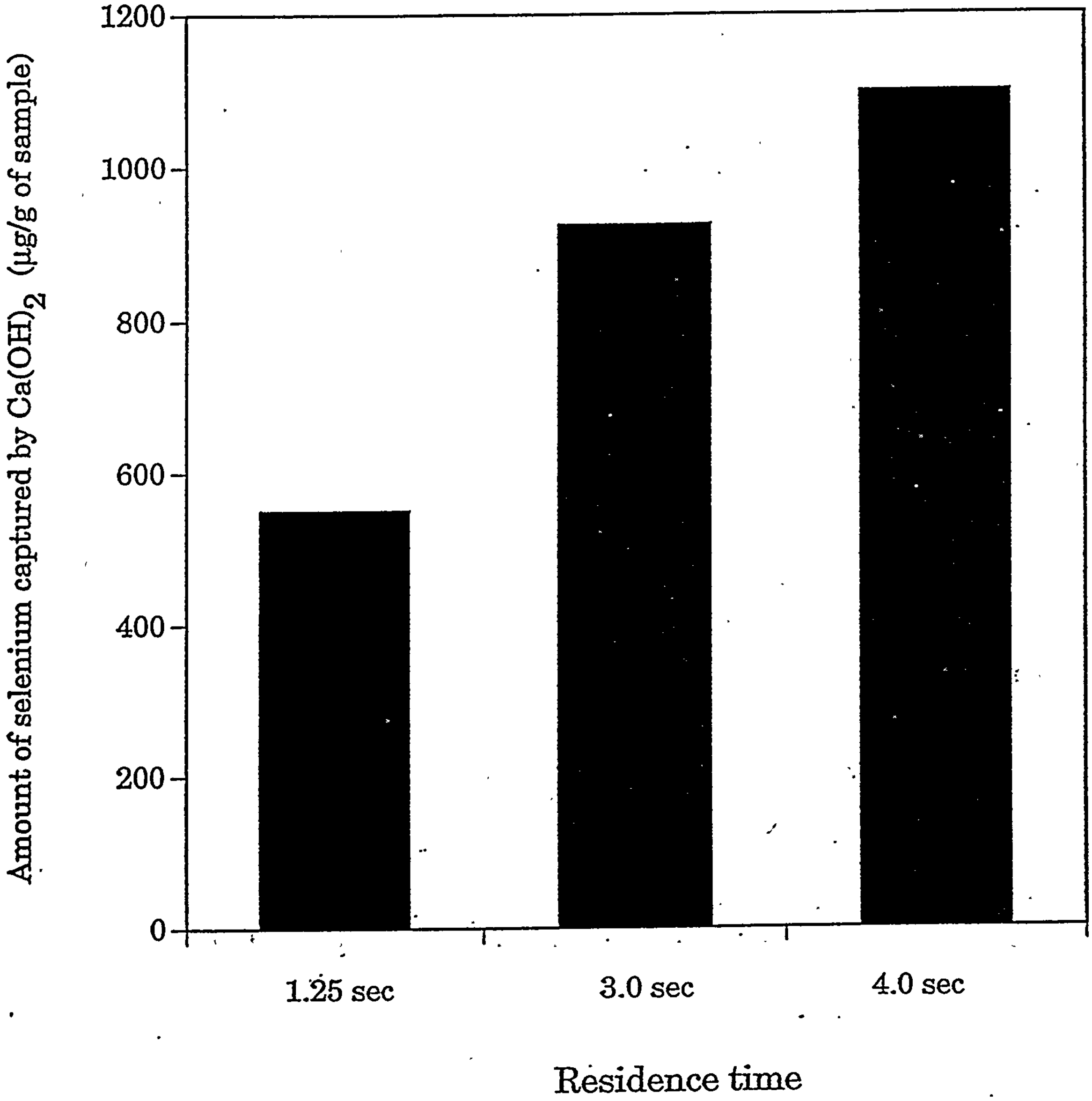


Figure 7: Amount of selenium captured by $Ca(OH)_2$ at different residence times in Entrained Flow Reactor. Selenium vapor phase conc. is 8 ppm and reaction temperature is 600°C

selenium vapor phase concentration of 8 ppm. As can be seen from the figure, at 1.25, 3.0 and 4.0 seconds residence times capture was 550, 925 and 1100 ppm respectively.

To determine the extent of selenium capture, if any, by the sorbent particles exposed to reactant gas in the cyclones at much lower temperatures than the reaction temperatures, a set of experiments was performed. These experiments consisted of two parts. During the first step of the experiments, $Ca(OH)_2$ was fed into the reactor at reaction conditions similar to the experimental conditions described earlier but in the absence of any arsenic species. After sufficient amount of sorbent powder was collected in the cyclones, powder feeding was stopped. the second step of the experiments involved starting the vaporization of the selenium dioxide in the absence of any powder flow. Selenium vapor phase concentration of 8 ppm was maintained throughout the second stage of the experiment. Vaporization was carried out for an hour (representative of the time spent by the captured partially reacted sorbent particles in an actual entrained flow experiment). Upon completion of the experiment, powder sample was recovered from the cyclones and analyzed for selenium content. Results from these experiments show a very low (less than 25 ppm) selenium capture by the partially calcined $Ca(OH)_2$ particles inside the cyclones, which is less than 5% of the selenium captured at a residence time of 1.25 seconds.

As can be see from the Figure 7, interaction between selenium vapor species and $Ca(OH)_2$ in entrained conditions does lead to a substantial amount of selenium capture by the sorbent powder. Selenium capture at low residence times (1-4 sec.) demonstrates the feasibility of Dry Sorbent Injection technique, with $Ca(OH)_2$ as the sorbent, in removing selenium species from the flue gas at medium range temperatures (450-650°C).

IV. INFLUENCE OF SO_2 ON SELENIUM CAPTURE BY $Ca(OH)_2$

In actual flue gas atmosphere Ca-based sorbents are exposed to various gaseous species including SO_2. The presence of SO_2 along with SeO_2, in the gas phase, could lead to various interactions. It has been postulated [8] that the presence of SO_2 along with SeO_2 would cause the reduction of SeO_2 species to Se. Interaction between $CaSO_4$ (formed as a result of SO_2/CaO) interaction) and SeO_2 could also lead to formation of complexes such as $SeOSO_4$ (selenium sulfate). All these interactions could greatly affect the selenium capturability of $Ca(OH)_2$.

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To determine the extent of selenium capture by the sorbent particles exposed to SO_2 and SeO_2, a set of experiments were performed under differential conditions. A differential bed of $Ca(OH)_2$ powder was inserted into the reactor and was precalcined at 600°C for about 30.0 min. after which it was exposed to the reactant gas containing SO_2 and SeO_2, at predetermined concentrations. SO_2 concentration was varied from 0 to 4000 ppm while SeO_2 concentration was maintained at 16 ppm for all the experiments. Results obtained from these studies are presented in Figure 8. As can be seen from these results, addition of SO_2 greatly reduces the amount of Se captured by the sorbent suggesting that the higher concentration of SO_2 in the gas phase causes preferential sulfation of the sorbent. The results also indicate that even though the SO_2 concentration was increased from 1000 to 4000 ppm the amount of sulfated sorbent remains nearly constant. Since the product of sulfation, $CaSO_4$, has a higher molar volume than CaO, these results would suggest extensive pore filling and complete reduction of porosity, as was confirmed later by the Bet analysis of the post-sorption sorbent sample.

In order to determine the selenium capture by $Ca(OH)_2$ without causing extensive sulfation and pore plugging, sorption experiments were also carried out at comparable SO_2 and SeO_2 concentration. Gas phase concentration of 130 and 300 ppm were maintained for SeO_2 and SO_2 respectively. As can be seen from the results shown in Figure 9, under comparable gas phase concentrations selenium capture substantially increases as compared the selenium capture at higher SO_2 concentrations. These results

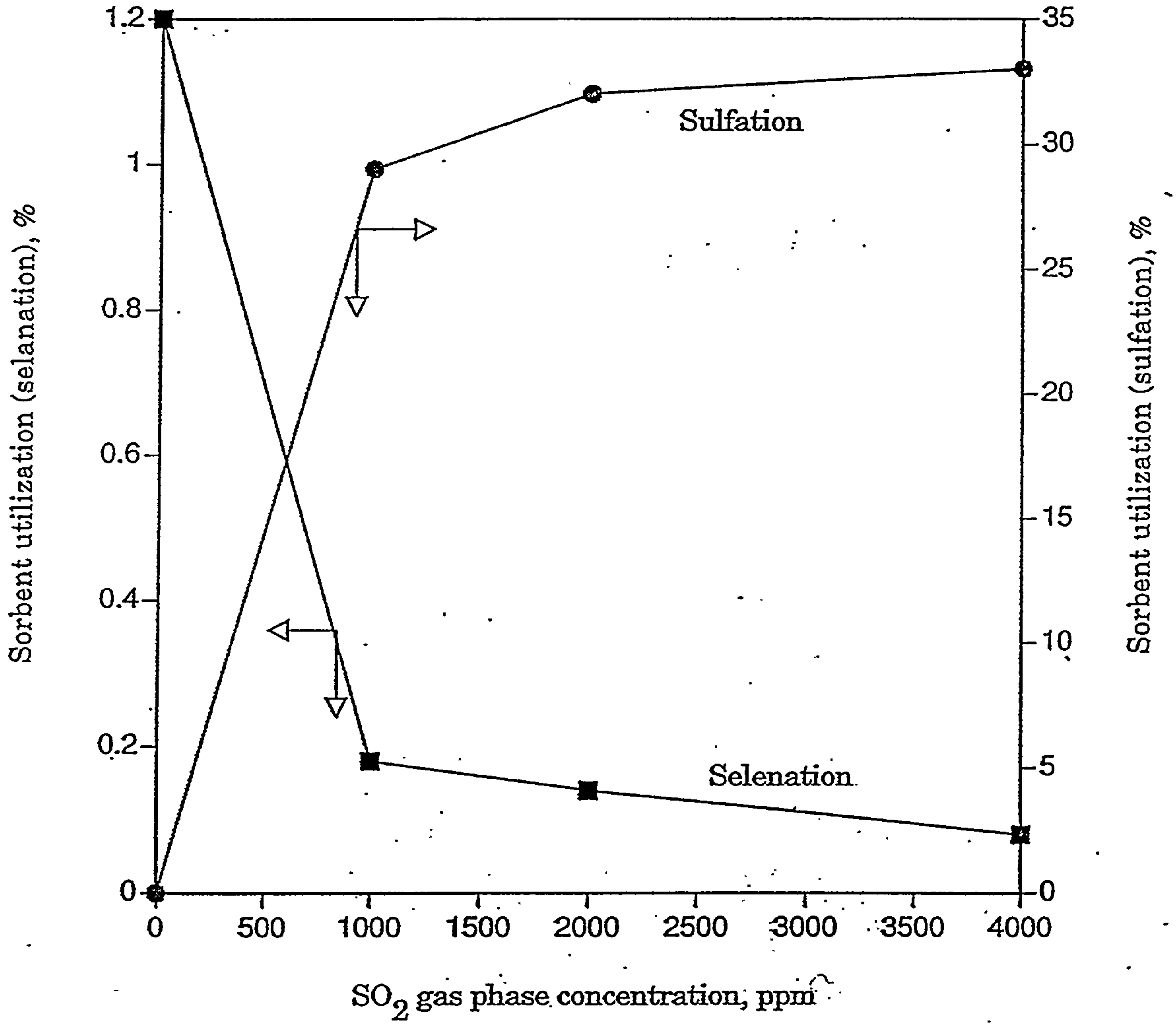

Figure 8: Effect of SO_2 concentration on selenium capture by $Ca(OH)_2$.
Sorption temperature : 600°C
Sorption time : 2 hrs.
SeO_2 gas phase conc. : 16 ppm

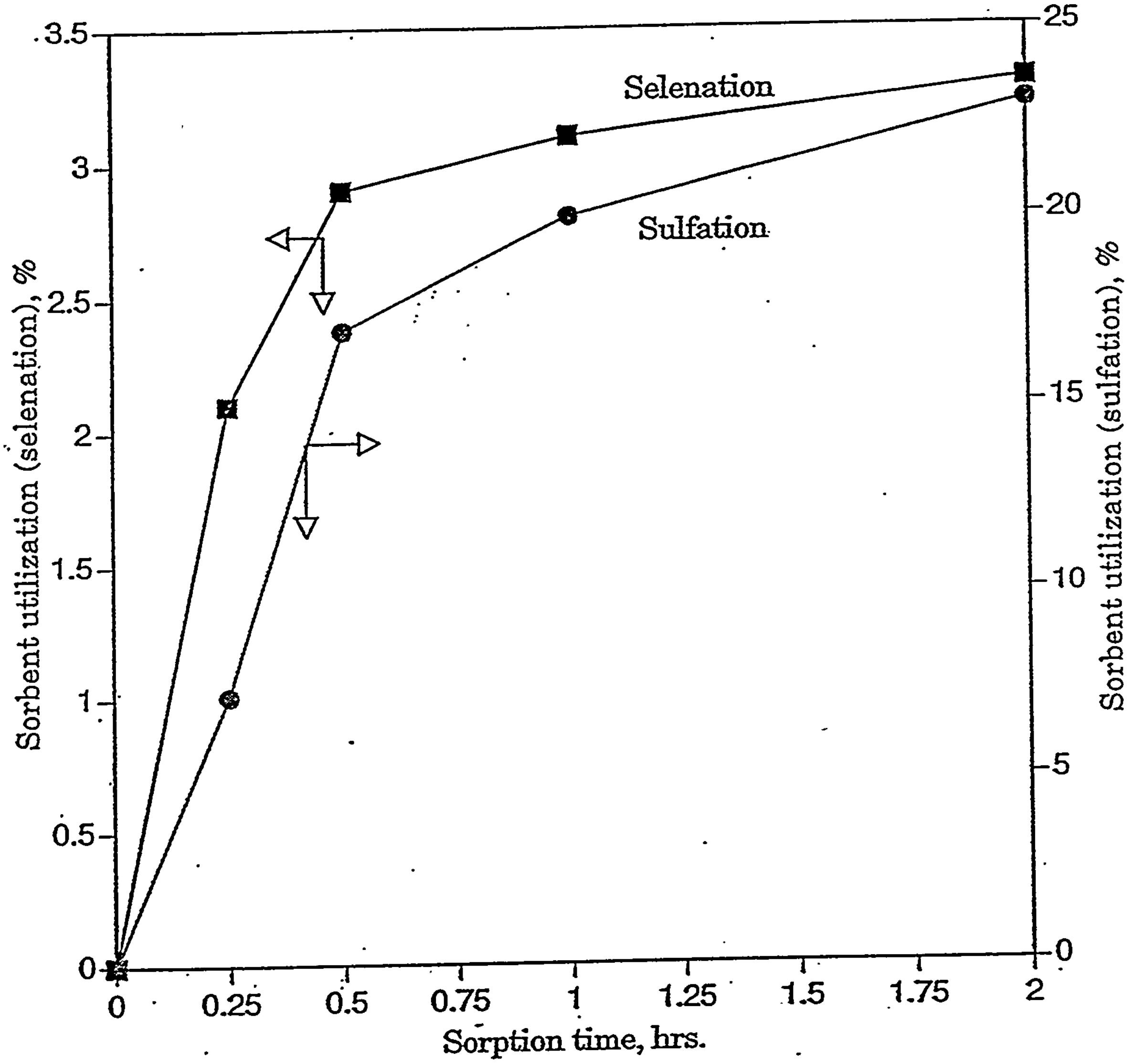

Figure 9: Extent of sulfation and selenation of $Ca(OH)_2$ with sorption time.
Sorption temperature : 600°C
SO_2 gas phase conc. : 300 ppm
SeO_2 gas phase conc. : 130 ppm

also suggest that the presence of SO_2 in the gas phase along with SeO_2 leads to independent sulfation and selenation of the sorbent.

Determination of SO_2 and SeO_2 gas phase reactions, if any, was carried out by conducting experiments without any sorbent bed at temperatures of 600°C and 200°C and gas phase concentrations of 130 and 300 ppm for SeO_2 and SO_2 respectively. It was found that at lower temperature (200°C) in the presence of water SO_2 did reduce SeO_2 to elemental Se, as is reported by [9] but at higher temperatures of interest (450-650°C) the reduction reaction was not found to be feasible.

V. CONCLUDING REMARKS

The major accomplishments of the second year of this project are as follows:

A thorough mechanistic investigation of the Se-Ca$(OH)_2$ interaction at both medium and high temperatures has been completed. and published as a paper entitled, "Selenium Capture using Sorbent Powders: Mechanism of Sorption with Hydrated Lime," to the *Environmental Science & Technology* journal. Experiments were performed in the two temperature ranges in the presence and absence of O_2; desorption studies were conducted to characterize the nature of interaction; and XRD/XPS and Ion Chromatography studies were performed for species identification. It was inferred from these findings that the selenium capture was significantly more in the medium temperature range (450-650°C) than in high temperature range (800-1000°C) and the captured selenium species in the medium temperature range is in the form of calcium selenite ($CaSeO_3$) and a reaction scheme was proposed for the CaO/SeO_2 interaction:

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$$CaO\,(s) + SeO_2\,(g) = CaSeO_3\,(s)$$

This reaction process does not require the participation of oxygen, as was confirmed by various analytical techniques and supported by the experimental evidence.

Results of the high-temperature studies indicate much reduced capture at these temperatures with negligible selenium sorption above 900°C. In contrast to the medium-temperature runs, results at these temperatures show a decreasing selenium capture by the sorbent as temperature increases. This behavior was attributed to the decomposition of calcium selenite at higher temperatures.

An Entrained Flow Reactor (EFR) system was designed and constructed in order to study the short time Se-Ca$(OH)_2$ interaction under entrained flow conditions. the EFR system was designed to conduct experiments with residence time in the range of 1-5 seconds and at temperatures upto 1000oC. Experiments were conducted in the EFR to test the capturability of selenium species by Ca$(OH)_2$. Results from these experiments indicate that Ca$(OH)_2$ captured as much as 1100 ppm of selenium species for a residence time of 3.0 seconds under entrained conditions. Thus suggesting the feasibility of Dry

Sorbent Injection technique in removing selenium species from flue gas by using calcium based sorbents.

In actual flue gas atmosphere Ca-based sorbents are exposed to various gaseous species including SO_2. The presence of SO_2 along with SeO_2, in the gas phase, could lead to various interactions. Experiments were conducted to determine the selenium capture by the $Ca(OH)_2$ sorbent, under differential conditions, in an atmosphere with containing SO_2. Results from these experiments indicate that $Ca(OH)_2$ interacts independently with SO_2 and SeO_2 (no significant gas phase interaction between SeO_2 and SO_2 in the temperature window of interest) in medium temperature range forming $CaSO_4$ and $CaSeO_3$ respectively.

VI. LIST OF REFERENCES

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