

Development of Disposable Sorbents for Chloride Removal from High-Temperature Coal-Derived Gases

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Introduction

The integrated coal-gasification combined-cycle approach is an efficient process for producing electric power from coal by gasification, followed by high-temperature removal of gaseous impurities, then electricity generation by gas turbines. Alternatively, molten carbonate fuel cells (MCFC) may be used instead of gas turbine generators. The coal gas must be treated to remove impurities such as hydrogen chloride (HCl), a reactive, corrosive, and toxic gas, which is produced during gasification from chloride species in the coal. HCl vapor must be removed to meet environmental regulations, to protect power generation equipment such as fuel cells or gas turbines, and to minimize deterioration of hot coal gas desulfurization sorbents.

Concentrations of HCl in coal gas have not been determined precisely, but they are estimated to be in the range 1 to 500 ppm (TRW, 1981). Bakker and Perkins (1991) point out that concentrations of HCl in coal gas can be about five times higher than those in coal-fired boiler combustion gas streams because of the lower volume of the coal gas. The actual concentration of HCl vapor in a coal gas stream will depend on the chlorine content of the coal, the gasification temperature, and the type of gasifier. Recently, (Bevan et al., 1994, 1995) measured the concentration of HCl to be about 300 to 600 ppm in a fixed-bed gasifier operating at 30 atm using Illinois #6 or a blend of Illinois #6 and Crown II coals.

The role of HCl as an impurity in coal gas used to fuel a gas turbine is not well defined and currently no concentration limit standards exist. In spite of the absence of specified limits, the removal of HCl vapor from the fuel can only be beneficial for IGCC systems, because the presence of HCl vapor is generally deleterious to the metal components of the IGCC systems. Perkins et al. (1990) report that the chloride deposits found on syngas coolers accelerate the corrosion of the heat exchanger material. HCl reacts with the deposited slags forming low-melting iron chlorides, and thereby accelerates the corrosion rate. For sustained and efficient operation of the MCFC, the feedgas must be free of chloride species. Halogen compounds are deleterious to MCFCs because they can lead to severe corrosion of cathode hardware (Kinoshita et al., 1988). HCl also can react

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with the molten carbonate electrolyte to form halides such as LiCl and KCl. The high vapor pressures of these compounds enhance electrolyte loss. An increase in the cell resistance and a corresponding decrease in the cell voltage were observed in feed gas containing 1 ppmv HCl vapor (Pigeaud and Wilemski, 1992). Hence, the allowable HCl concentration in a MCFC feedgas is estimated to be less than 0.1 ppmv.

A number of processes are available for removing HCl vapor from industrial and incinerator waste gases. These processes scavenge HCl by adsorption onto activated carbon or alumina or by reaction with alkali or alkaline earth carbonates or oxides. In chemical plants where HCl must be removed from process feedstocks, commercial sorbents called chloride guards are marketed by catalyst manufacturers and these sorbents are relatively expensive. These sorbents reduce chloride contaminant levels to <1 ppm, but they must operate at temperatures <450°C. Furthermore, none of them are economically regenerable. Hence, inexpensive and disposable sorbents are needed for the chloride removal in hot coal-derived gas streams.

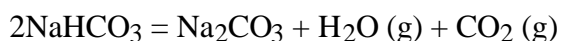
Objectives

The objectives of this study are to: (1) investigate methods to fabricate reactive sorbent pellets or granules that are capable of reducing HCl vapor in high-temperature coal gas streams to less than 1 ppm in the temperature range 400° to 650°C and the pressure range 1 to 20 atm; (2) testing their suitability in bench-scale fixed- or fluidized-bed reactors; (3) testing a superior sorbent in a circulating fluidized-bed reactor using a gas stream from an operating coal gasifier; and (4) updating the economics of high temperature HCl removal.

Approach

Equilibrium thermodynamic calculations showed that only sodium and potassium compounds are capable of reducing HCl vapor levels to less than 1 ppm level at 527°C. Potassium compounds are capable of achieving the lowest HCl vapor levels, but the vapor pressure of KCl(g) exceeds that of NaCl(g). If potassium compounds are to be used for HCl removal, then the release of alkali vapor in the hot coal gas could be higher than the case in which sodium compounds are used. The sodium minerals are more abundant than potassium minerals in nature. Hence, the use of sodium minerals are preferable as disposable sorbents for HCl removal.

Of the major sodium minerals in the U.S., nahcolite (NaHCO₃) mineral is suitable for the HCl removal applications. Approximately 30 billion tons of nahcolite minerals occur in the Piceance Creek Basin of northwestern Colorado and of these, 17.5 billion tons could be recovered economically (Farris and Mains, 1978). Nahcolite is converted to soda ash on heating to a temperature above 150°C:



The release of steam and CO₂ results in a porous and reactive sorbent. At the temperature of interest, HCl reacts with Na₂CO₃ to form NaCl:



Previous studies demonstrated that nahcolite is capable of high HCl reactivity and high chloride capture capacity (Krishnan et al., 1986). Bench-scale experiments showed that the HCl vapor level were reduced to less than 1 ppm in the temperature range 400° to 550°C and chloride loading levels in the spent sorbent could be as high as 50 wt%.

The sorbents can be used in fixed-, fluidized, or moving-bed reactors. In fluidized-bed reactor applications, the fresh sorbent can be introduced pneumatically at the outlet of the gasifier and the spent sorbent can be collected along with the coal ash in a cyclone (Bevan et al., 1994). This simple reactor concept is adequate for applications in which HCl level should be low. However, for MCFC applications where the residual level of HCl level must be less than 1 ppm, fixed- or moving-bed reactors are needed to provide sufficient contact time. In a guard-bed mode, the fixed-bed reactors could be relatively compact or the sorbent pellets need to be changed only after a relatively long period of time. An economic evaluation using fixed-bed reactors for HCl cleanup indicated that the use of nahcolite to remove HCl vapor would add only about \$0.002/kWh (2 mills/kWh) to the cost of the generated electric power (Krishnan et al., 1986).

Project Description

Bench-scale, cylindrical stainless steel pressure vessels, capable of operating at temperatures up to 923 K (1202°F) and pressures up to 20 atm, were used for both fixed-bed (at SRI) and fluidized-bed (at RTI) tests. The sorbent beds were contained in 5-cm ID quartz tubes mounted inside the pressure vessels. To minimize corrosion, only the non-corrosive components of the simulated coal gas mixtures could come into contact with the stainless steel walls. HCl and H₂S were introduced directly into the quartz tube, upstream of the sorbent bed. Pressure was controlled by a Hastelloy servocontrolled valve at the outlet of the pressure vessel. The reactor effluent was cooled in a heat exchanger made of glass, wherein residual HCl vapor dissolved in the steam condensate. The chloride level in the condensate, determined by ion chromatography, provided a measure of the residual HCl vapor concentration. This procedure is capable of measuring sub-ppm levels of HCl vapor.

Several sorbent pellets made by extrusion using nahcolite powder (obtained from NaTec Resources, Inc., Houston, Texas) and bentonite or sodium silicate binders. These pellets, in the size range 1.5 to 4 mm, were used for fixed-bed reactor testing. For the fluidized-bed reactor studies, nahcolite sorbent granules (40 to 150 μm in size) with kaolinite and bentonite binders were made using a spray dryer. A simulated coal gas composition representative of Texaco oxygen-blown gasifier was used in the bench scale studies. The HCl level was set arbitrarily at a high level of 1750 ppm. The H₂S and H₂O levels were typically 3000 ppm and 25 vol%, respectively.

In addition to the bench-scale tests with simulated gas, a small batch of the spray-dried sorbent was also tested at the pilot-scale fixed-bed gasifier facility located at the General Electric Corporate Research and Development site.

Results

Experimental tests were conducted during the previous years in this program (Krishnan et al., 1994; 1995) provided the following results:

- No significant differences in the HCl reactivity were observed between sodium silicate and bentonite binders. At a space velocity of 3000 h⁻¹, the HCl level was reduced from 1750 ppm to less than 1 ppm and the maximum chloride content of the spent pellets was about 55 wt%. The maximum chloride capacity of the pellets with sodium silicate binder was 10% higher than that of the pellets with bentonite binder, but the rate of initial reaction did not depend strongly on the nature of the binder.

- Pellets containing sodium silicate binder agglomerated when the reaction temperature was higher than 500°C. No such agglomeration was observed when bentonite was used as the binder.
- The crush strength of the pellets made with nahcolite was comparable to that of zinc titanate desulfurization sorbents and it did not change significantly with the extent of chlorination.
- The sorbents prepared by spray-drying have a superior reactivity and chloride capacity than the raw nahcolite powder. The attrition resistance of the spray-dried sorbent was comparable to that of a commercial FCC catalyst.
- Experiments in a 2.5-cm diameter fluidized-bed reactor showed that the spray-dried sorbent also has a high reactivity for HCl and a high chloride capture capacity. The residual HCl level was less than 1 ppm at 550°C with spent sorbents containing as high as 50 wt% chloride indicating nearly complete capacity utilization.
- The presence of H₂S did not affect the HCl reactivity or the chloride capacity of the sorbent under atmospheric pressure conditions.

Recent experiments focussed on experiments at elevated pressures. Fixed-bed reactor experiments with simulated coal gas containing both HCl and H₂S vapor showed similar results as with atmospheric pressure runs. As shown in Figures 1 and 2, the residual HCl level remained below 1 ppm and the HCl breakthrough occurred at periods longer than 20 h.

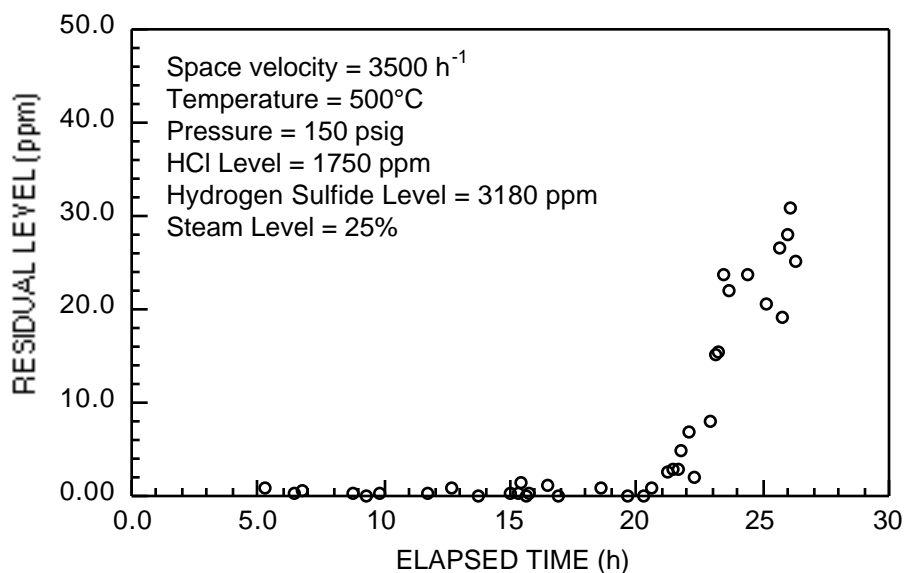


Figure 1. The residual HCl level as a function of reaction time.

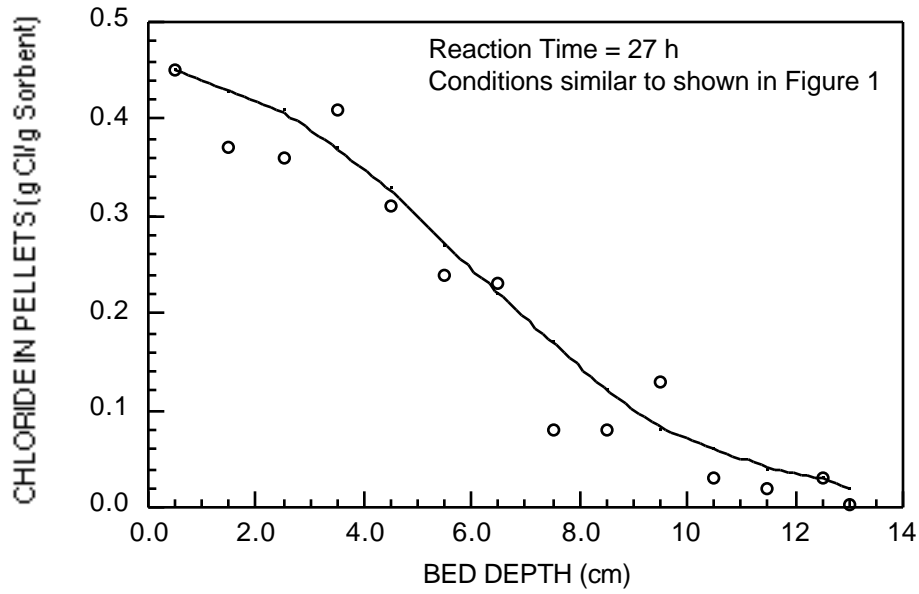


Figure 2. The chloride content of the pellets as a function of bed depth.

Experiments were also conducted with pellets made from trona ore ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3$) at 1 atm. However, the reactivity and chloride capacity of trona pellets were significantly inferior than those of nahcolite pellets (Figure 3). Similar results were also found in tests with fluidized-bed reactors.

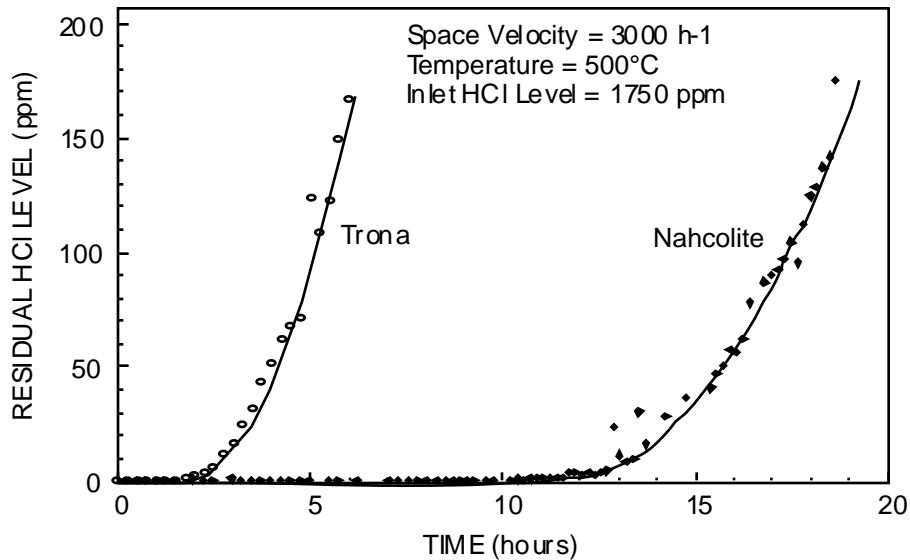


Figure 3. Comparison of HCl removal by trona and nahcolite pellets at 1 atm.

A fluidized-bed reactor test was also conducted with a commercial sorbent made by United Catalyst, Inc. The UCI sorbent also reduced HCl level to less than 1 ppm, but its chloride capacity was significantly less than that nahcolite pellets (Figure 4). This result is expected, because the UCI sorbent is made for guard bed applications rather than for bulk removal of HCl vapor.

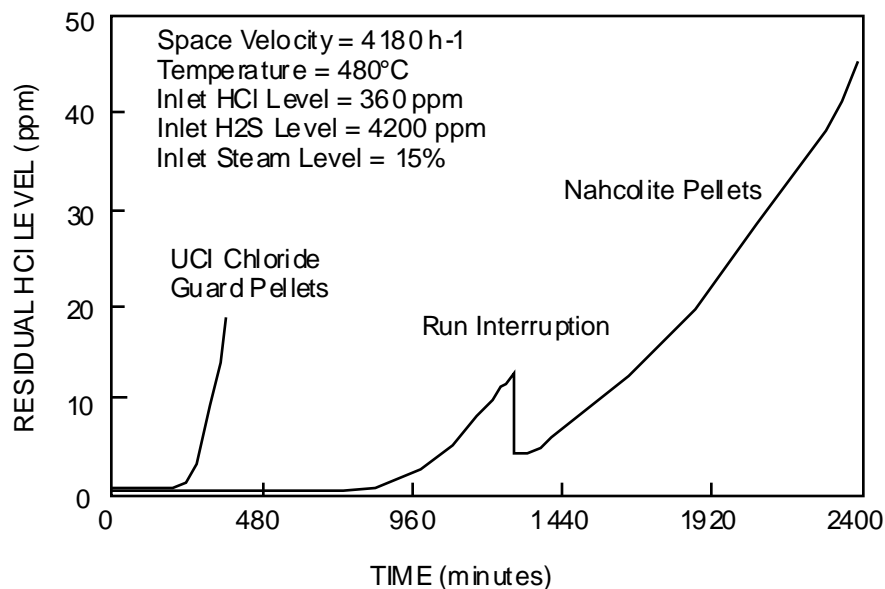


Figure 4. Comparison of HCl removal by a commercial chloride guard and nahcolite pellets.

A preliminary pilot-run at the GE fixed-bed gasifier facility using their circulating fluidized-bed facility showed that both sodium carbonate and spray-dried sorbent could reduce the HCl level in the hot coal gas stream from about 580 ppm to less than 15 ppm (Figure 5). Grade #2 sodium bicarbonate powder was used as the HCl removal sorbent during the initial 110 h. The sorbent was injected into the reactor pneumatically using a nitrogen carrier gas. The initial residual HCl level was somewhat high due to low sorbent level in the reactor. As the bed inventory was increased, the HCl removal efficiency increased. During the last 5 h of the test, the Grade #2 sodium carbonate was replaced with 100 lbs of spray-dried nahcolite granules supplied by RTI. The calculated HCl removal efficiency was greater than 97% with both sorbents. The spent spray-dried sorbent contained as much as 38 wt% chloride, corresponding to a sorbent utilization of 71%.

The spray-dried sorbents before and after coal gas exposure were analyzed to determine whether any trace element species present in the hot coal gas stream would be retained. As shown in Table 1, B, Pb, and Zn species were significantly higher in the spent sorbent than in the the original sorbent. The data is insufficient to conclude that the observed increase in the levels of Cd, Mo, and Cu is significant. The trace metal species accumulated on the spent sorbent could be either from the trace metal vapors adsorbed or reacted with the sorbent or fine ash particles retained in the sorbent bed. Additional tests are needed to determine the origin and extent of trace element species that accumulate on the sorbents.

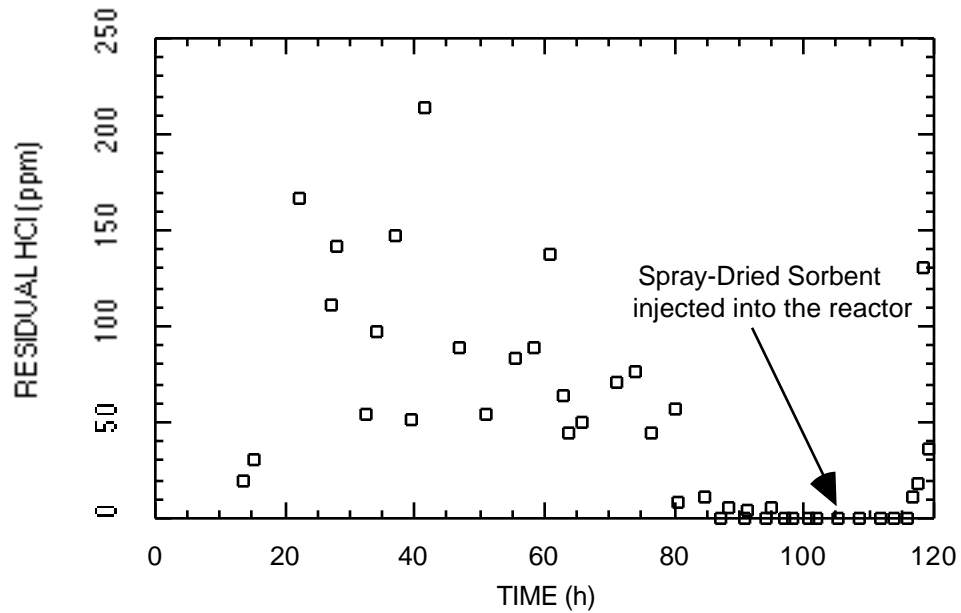


Figure 5. The residual HCl vapor level in the pilot-scale test with sodium bicarbonate powder and spray-dried sorbent.

Table 1. Concentrations of Trace Elements in the Original and Coal-Gas Exposed Spray-Dried Sorbent

Element	Concentration in Original Sorbent (ppm)	Concentration in Spent Sorbent (ppm)
B	<15	1425
Ba	41	42
Be	<1	<1
Cd	<3	5
Cr	15	<10
Cu	<10	22
Pb	<15	1065
Mn	<10	<10
Mo	<15	<30
Ni	<15	<15
Sr	31	30
V	30	30
Zn	65	145

A second gasifier gas stream test using a 400 kg of spray-dried sorbent was scheduled in March 1996. An improved sorbent was prepared for this test. However, difficulties were encountered in feeding the sorbent because of bridging in the feed hopper.

Applications

The results of the current program have demonstrated that HCl vapor can be removed from coal gas streams at elevated temperatures using disposable, inexpensive, naturally occurring minerals. The HCl vapor in the gas could be reduced to levels required to meet environmental regulations and MCFC applications. This technology results in a dry process with minimal amount of a solid waste to be disposed of. The alternative technology, which is the current practice, is to quench the coal gas with water and remove the HCl vapor in the aqueous solution. The waste solution is more difficult to dispose than the solid waste.

Future Activities

Future activities in the program include preparation of about 400 kg of spray-dried sorbent for another pilot-plant test, parametric testing of the sorbents in a bench-scale fluidized-bed reactor, and a preliminary economic assessment of the chloride removal process.

Acknowledgments

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