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# Limestone's performance as a solid adsorbent for HF and HCl generated in refrigerant destruction applications

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**Abstract**−The viability of two solid adsorbents, limestone and cement powder, for use in a flow-through packed-bed column for HCl and HF gas neutralization following refrigerant destruction was studied. Neutralization tests performed at 408 K using 5% HCl in $N_2$ and 5% HF in $N_2$, showed that limestone had a significantly higher adsorption capacity for both HF and HCl. ~49% of fed HCl, and between 7.8%-16.2% of fed HF gases were adsorbed by 7 g of limestone for a gas flow rate of $6.67\times10^{-6}$ $m^3/s$ (STP) over 30 to 180 minutes. Effective diffusivities ($D_e$) of HCl and HF into the limestone particles were $1.5\times10^{-9}$ and $2.2\times10^{-9}$ $m^2/s$, respectively, indicating that a solid diffusion mechanism dominance would limit the suitability of this method as a solid adsorbent in the tested form. Under these conditions, complete particle conversion times were 227 hours for HCl-limestone and 154 hours for HF-limestone. Considering the long conversion times observed, shorter conversion times would require micron-scale particle sizes, suitable for entrained flow but not for a packed-bed arrangement. A $Na_2CO_3$/Limestone slurry used to neutralize the reactor effluent proved efficient within this system, and may be a more suitable alternative for acid neutralization involving HF.

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Keywords: HF, HCl, Refrigerant Destruction, Solid Adsorption Media, Shrinking Core Model

## HIGHLIGHTS

- Cement powder was found to be an unattractive solid adsorbent for acid gas treatment due to low uptake
- Low rates of HCl and HF acid gas adsorption and neutralization by limestone particles at moderate temperatures (140 °C) would present significant challenges in designing a solids-based gas treatment platform
- Shorter conversion times would require entraining the particles in the gas flow for the neutralization to occur.
- Slurry-based neutralization system incorporating $Na_2CO_3$ and limestone produced gas effluents below detection limits of Honeywell MDA Scientific Midas monitor (sub ppm)

## INTRODUCTION

Aspects of the Montreal Protocol governing the phase-out of ozone-depleting refrigerants such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) has led to the development of a number of alternative refrigerants for use in legacy equipment and new applications [1]. There continues, however, to be a need for CFC and HCFC compounds to service equipment nearing end-of-life or requiring small refrigerant quantities for on-going maintenance. This has led to the development of refrigerant reclamation industries focused on reprocessing waste mixed refrigerants to provide a recycled product without the additional generation of CFC's. Refrigerant Services Inc. (RSI) in Dartmouth, NS, Canada, operates one of the few reclamation facilities in Canada, generating as part of their process approximately 12 tons per month of highly contaminated and diverse waste refrigerant stream which currently must be shipped via rail car to either Alberta or Texas for disposal. This disposal is currently subsidized by regulatory surcharges placed on refrigerants, which could act as an alternative revenue stream if performed in-house. One aspect of considering this process is the potential to produce value-added products which could be re-sold to local industry, primarily in the form of fluorinated particulates.

Halocarbon destruction methods have historically been classified as chemical, thermal or electrically based, with the most predominant method being injection into operational cement kilns [2]. Plasma technology has more recently been considered as an alternative for small scale applications, being a hybrid method combining thermal and electrical aspects of traditional destruction techniques. They are being increasingly considered as a viable alternative to cement kiln destruction of CFC/HCFC compounds [3]. Their advantages include the use of electricity as a power source, resulting in more process chemistry options, fine control of the process environment and rapid shut-down options, lower off-gas flow rates, and thus lower gas cleaning costs, the possibility of producing marketable co-products, and the presence of high energy densities and temperatures which permit rapid heating and reactor startup, high heat and reactant transfer rates, smaller installation sizes and high quench rates [4]. As with most decomposition-based method of disposal for CFC's, the plasma process generates hydrochloric and hydrofluoric acids at moderate concentrations in the effluent streams [5]. Both of these acids are hazardous to human health, with exposure limits in the range of a few ppm. The traditional process for neutralizing these gases involves wet chemistry with caustic solution which, while efficient, limits alternative chemistry options when a value-added product is

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being sought. Solid-based adsorption and neutralization may offer opportunities to potentially provide a production means for value-added fluorinated products if introduced directly within the plasma stream or present as an adsorbed following refrigerant decomposition. An example of such a process was recently presented by Yasui et al. [6], who studied gas solid reactions between alkaline solid adsorbents and the effluent of a steam reformer destroying refrigerants. The reported performance and particle utilization appeared promising for the high steam ratios present within their system, but they did not provide details on how limited moisture content would affect the kinetics of the system. HF and HCl gases have a tendency to passivate solid surfaces, which can significantly affect an adsorbent's ability to neutralize the flowing media. The presence of moisture can have a significant impact on the acidic activity of HF and HCl gases, mitigating the effects of passivation on solid adsorbent performance. To provide RSI with a realistic assessment of potential adsorption kinetics with limited moisture presence in the stream, additional information regarding the kinetics of neutralization was needed.

Our objective was thus to explore the feasibility of a locally supplied limestone particulate as a solid adsorbent for the neutralization of effluent acidic gases carried by a dry gas stream. This was done exposing limestone in an electrically heated tubular furnace to flows of either 5% HCl or 5% HF acid gases in $N_2$ and determining effective diffusivities based on the shrinking core kinetic model to provide a means of assessing process scalability and adsorption capacity.

## EXPERIMENTAL METHODOLOGY

Given the nature of the gases employed in this study, a significant focus must be placed on the safety requirements inherent in working with these materials.

The experimental system (Fig. 1) was constructed to enable either pulsed or continuous injection of acid gases through an electrically heated tubular reactor, with effluent acid gas concentrations monitored through the use of an ion-selective probe (Cl- or F- selective depending on the process gas) placed in the downstream reservoirs. All materials in contact with the acid gases were constructed of either Monel or Inconel 600. During each run, the neutralization reservoirs were loaded with either a sodium bicarbonate slurry (for HCl runs) or a bi-composite sodium bicarbonate/limestone slurry (for HF runs), and mechanically agitated while cooled to enhance gas/liquid mass transfer. A custom-built tubular reactor (2.54 cm ID) was loosely packed with ~7 grams of target solid media, retained by a 100-Mesh Monel wire screen. After being sealed with Deacon 8875-Thin high temperature sealant and loaded into an electric furnace (John Deere, 2238-24-3ZH), the system was heated to 250 °C and purged with nitrogen to drive out residual moisture and oxygen within the system. Leak testing was also performed at this time.

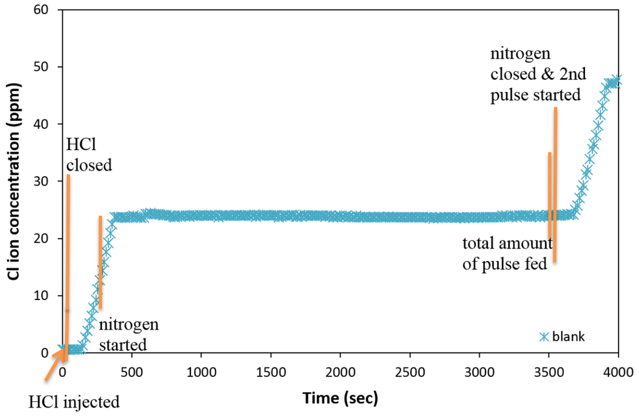

**Fig. 2. First pulse of the breakthrough curve for a blank run showing important procedural points.**

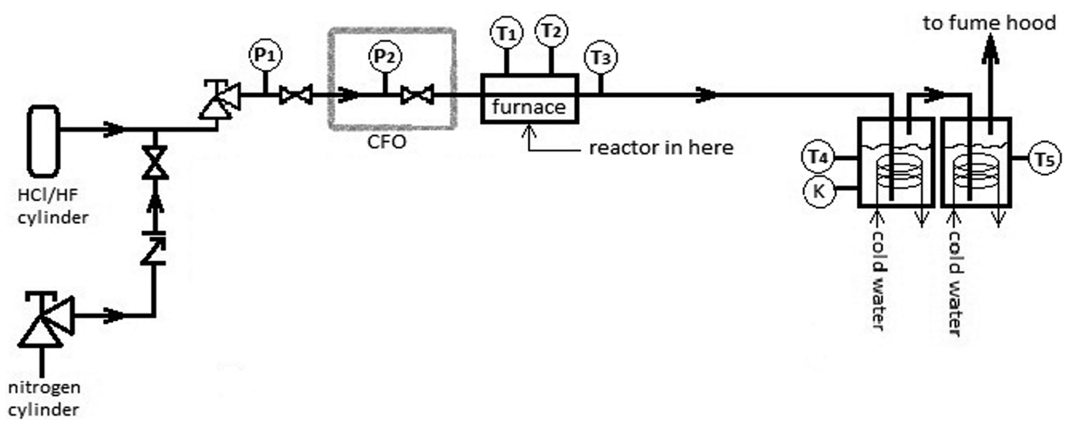

**Fig. 1. Schematic diagram of the acid gas neutralization system using solid adsorbents.**

Due to the high cylinder pressure present for the HCl (~1600 psi), pulsed injections were then introduced by briefly charging the T-purge assembly volume of the regulator (Matheson Gas, 3215-330) to the cylinder pressure, after which the cylinder was closed and the system allowed to depressurize through the regulator for a downstream set pressure of 40 psi (Fig. 2). For the HF experiments, the shipped cylinder pressure was only 140 psi, necessitating continuous injection with the cylinder valve open. Flow of the gas to the reactor was controlled at 350 sccm via a calibrated critical flow orifice equipped with an upstream Monel test gauge (Omega PGT-45B-60). Such a significant flow rate was chosen to minimize external mass transfer resistance around the solid particles and partially fluidize the system to avoid packed-bed behavior, thereby emphasizing the neutralization kinetics of the solid as the dominant factor governing the composition of the effluent stream. Effluent gas temperatures were found to repeatedly reach 135 to 140 °C at the exit point of the furnace, at which the gas was routed to a series of caustic baths for neutralization.

Two polypropylene baths equipped with internal cooling coils and magnetic stirrers were employed both for neutralization and monitoring of acid content of the reactor effluent stream. HCl and HF ion selective probes (Cole Parmer K-27502-07 and K-27502-19, respectively) were calibrated for use within the neutralizing solutions, subject to the solubility expectations of the neutralization products produced. For the HCl experiments, a homogeneous solution was employed, whereby the solubility limit of the neutralization product (NaCl) was not exceeded, allowing for direct measurement of chloride ions in solution. For the HF experiments, NaF was formed as an intermediate compound within the neutralization process to enable on-stream fluoride ion concentration measurement, and was slowly converted to $CaF_2$ by the limestone present in the slurry to provide a precipitated product which also offering a secondary measurement of cumulative fluoride adsorbed through the change in mass of the solid particles in the system (following filtration and drying). In all experiments, headspace measurements performed in the first reservoir using Honeywell's MDA Scientific Midas gas detector indicated that effluent acid gases from the reactor were completely adsorbed by the first reservoir (i.e., sub ppm levels), which was also confirmed through ion content measurement of the second reservoir's media.

Following gas injection, solid media from the reactor was weighed, partitioned and dissolved in water volumes appropriate to ensure solubility levels were not exceeded. Following dissolution, the ion selective probes were used to determine the chloride and fluoride content as appropriate. For some of the later experiments, the net mass of solids remaining in the reactor following gas exposure was monitored as a secondary confirmation of the measured chloride/fluoride content determined by the ion selective probes.

During operation of the system, the Midas gas detector was first tested through a controlled exposure to the gases employed, then continuously used to actively monitor for gas leaks. Access to the lab was limited, with any personnel present being required to wear respirator protection. The neutralization reservoirs were also placed within a fume hood as a secondary mitigation of the effluent stream. A calcium gluconate supply was maintained in the lab in the event of a spill of the neutralization reservoirs.

## RESULTS AND DISCUSSION

Neutralization tests were initially performed using HCl for three ranges of limestone particle radii, R, obtained from sieving: 0.298<R<0.584 mm, 0.584<R<0.625 mm and 0.625<R<1.18 mm. Each test involved a sequence of three pulsed injections before the neutralization capacity of the reservoir was approached, with typical reservoir concentration responses illustrated in Fig. 3. For each series of three injections, the cumulative HCl injected within each pulse was determined from the combined chloride content in both the reservoirs and reactor, as well as through comparison to repeated blank runs performed at multiple points within the experimental program. Typical pulsed injections resulted in 0.0050 moles of HCl fed in total over the three injections, with variances in the relative fractions per pulse ranging from 32.8% to 34.2% (corresponding to net injections of 0.00165 to 0.00171 moles HCl per pulse). The response curves from the reservoir were then used to determine the differential quantity of HCl adsorbed in each pulse.

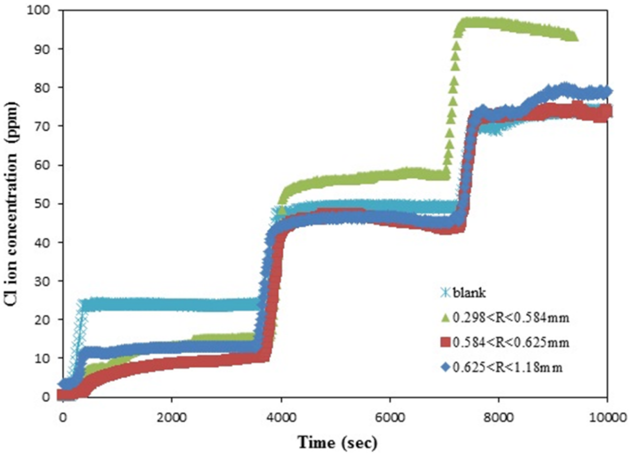

**Fig. 3. Typical reservoir concentration response curves for HCl pulsed injections in the absence of particles (blank), and for particle sizes of 0.298<R<0.584 mm, 0.584<R<0.625 mm and 0.625<R<1.18 mm.**

The particle density of the Mosher pelletized limestone was determined experimentally via displacement methods, whereby a measurable mass of particles was added to a volume of saturated slurry solution and the volume change rapidly recorded to estimate the average particle volume. This assumes that the particles pores are minimally wetted within a short time frame, and that no volume will be lost due to dissolution by the suspending phase. The particle density was measured to be 1,501 kg/$m^3$, compared to a general range of 1,444 to 1,926 kg/$m^3$ reported by Mosher. Based on a reported specific gravity of 2.7 to 2.95, the porosity would be within the range of 45 and 50%. The commercial assay for the limestone indicated a fairly broad range of compositions depending on source, with $CaCO_3$ content ranging from 50 to 95 wt% (MW of 100 g/mol), and $MgCO_3$ content ranging from 4 to 40 wt% (MW of 84.3 g/mol). Given that both of these compounds will react with the acid gases in question and that calcium carbonate is the primary component present, the MW of calcium carbonate was used to establish a conservative molar capacity for the solid particles (15,010 mol/$m^3$ particle).

Knowing the molar capacity, the volume of particles which would be needed to neutralize the quantities of HCl adsorbed during each pulsed run was determined. Considering the significant upward velocity of the gas through the small reactor bed and the loose packing used, the particles were assumed to be both well mixed with negligible external mass transfer resistance. As such, interpretation of the neutralization focused primarily on internal phenomena within the particle. The absence of significant delay between the initial pulse injection and the response from the reservoir indicated that the bed was more fluidized than packed, simplifying the analysis to that of a well-mixed reactor within which shrinking core kinetics can be applied [7-14].

$$t=\frac{\rho_B R^2 \phi_C}{6bD_e C_{As}}\left[1-3\left(\frac{r_c}{R}\right)^2+2\left(\frac{r_c}{R}\right)^3\right] \tag{1}$$

where $\rho_B$ is the molar density of $CaCO_3$ and has a value of 15,010 mol/m$^3$ $CaCO_3$ based on a limestone density of 1,501 kg/m$^3$, $\phi_C$ is the volume fraction of $CaCO_3$ in the particle assumed to be 1, b is the stoichiometric coefficient of the solid in the chemical reaction between calcium carbonate and HCl/HF having a value of 0.5, $C_{As}$ is the bulk phase concentration of HCl or HF (assumed to be constant at 5% by volume at a pressure of 101,325 Pa and temperature equivalent to that of the effluent gas) with a value of 1.5 mol/m$^3$, and $r_c$ and R are the unreacted front position and outer radius of the particle, respectively, whose values are estimated from the volume of particle reacted via the measured chloride/fluoride ion content of the solids. The time was measured experimentally and the radius estimated based on the fraction of solid consumed by the acid gas and the initial radius of the particles. $D_e$ is the effective diffusivity value for the acid gas into the limestone particle and was obtained by using Eq. (1).

Approximately 49% of the fed HCl and between 7.8%-16.2% of the fed HF gases reacted with the limestone particles in the reactor. The effective diffusivities of the HCl and HF gases into the limestone particles as obtained using the shrinking core model were estimated to be $1.5\times10^{-9}$ m$^2$/s and $2.2\times10^{-9}$ m$^2$/s, respectively, at 408 K, and $5.61\times10^{-9}$ m$^2$/s and $8.24\times10^{-9}$ m$^2$/s respectively at 873 K. These effective diffusivity values result in complete particle consumption times of 227 hours and 154 hours for HCl and HF, respectively, at the experimental conditions, and 61 hours and 41 hours, respectively, under the microwave plasma conditions. Cement powder was found to adsorb only 0.65% of the fed HF gas when compared to the 1.16% adsorbed by limestone under the same experimental conditions.

The theoretical $D_e$ values under the experimental conditions were calculated using Eq. (2) [15]. This equation shows a linear correlation between the bulk diffusivity ($D_{AB}$) and effective diffusivity ($D_e$), which is dependent on the pore properties of the particles.

$$D_e = \frac{D_{AB}\phi_p\sigma_c}{\tau} \tag{2}$$

where $D_{AB}$ is the diffusion coefficient of the gaseous mixture in cm$^2$/s, $\phi_p$ is the pellet porosity assumed to be 0.4, $\sigma_c$ is the constriction factor assumed to be 0.8 and $\tau$ is the tortuosity assumed to have a value of 3.0. The diffusion coefficient ($D_{AB}$) of a binary gaseous mixture was found by using the modified Chapman-Enskog [16].

$$D_{AB} = \frac{0.00266T^{3/2}}{PM_{AB}^{1/2}\sigma_{AB}^2\Omega_D} \tag{3}$$

Using Eqs. (2) and (3), together with the values provided in Table 1, the effective diffusivities ($D_e$) and the time for complete particle reactions for the two gaseous mixtures in limestone were estimated.

To estimate the $D_e$ values at plasma reactor temperatures i.e. 873 K, we assumed that the properties of the gas and the solids remained unchanged at 873 K. In which case the value of the constant of proportionality from Eq. (2), calculated as the ratio of the effective diffusivity to the bulk diffusivity for HF, would be $5.7\times10^{-5}$.

**Table 1. Parameter values used to calculate diffusion coefficients of HCl and HF in nitrogen [16]**

| Mixture | $M_{AB}$ g/mol | $\sigma_{AB}$, Å | $\Omega_D$, K | P bar | T K | $D_{AB}$ (m$^2$/s) |
|---|---|---|---|---|---|---|
| HCl in $N_2$ | 31.68 | 3.56 | 0.98 | 1 | 408 | $3.11\times10^{-5}$ |
| HF in $N_2$ | 23.34 | 3.46 | 0.98 | 1 | 408 | $3.86\times10^{-5}$ |

**Table 2. Estimated time for complete reaction of limestone particles with HCl**

| | $D_e$ (m$^2$/s) | Particle size range (mm) | Time (hrs) |
|---|---|---|---|
| Experimental $D_{e\ avg\ radius\ at\ 408\ K}$ | $1.5\times10^{-9}$ | 0.625<R<1.18 | 505.95 |
| | | 0.584<R<0.625 | 226.99 |
| | | 0.298<R<0.584 | 120.67 |
| Projected $D_{e\ avg\ radius\ at\ 873\ K}$ | $5.61\times10^{-9}$ | 0.584<R<0.625 | 60.51 |
| Theoretical $D_{e\ at\ 408\ K}$ | $3.13\times10^{-6}$ | 0.625<R<1.18 | 0.23 |
| | | 0.584<R<0.625 | 0.10 |
| | | 0.298<R<0.584 | 0.05 |

The effective diffusivity values obtained can be seen to vary from the theoretically calculated value by several orders of magnitude (Table 2). The three-fold reduction in order of magnitude relates change from pore diffusion dominated mass transfer resistance to solid diffusion dominated resistance.

The theoretical values on the order of $10^{-6}$ represent the diffusion occurring into the pores, and does not account for the increased resistance encountered as the HCl reacting front actually recedes into the limestone solid itself. Eq. (2) shows that there is a linear correlation between the bulk diffusivity ($D_{AB}$) and effective diffusivity ($D_e$). The linear relationship from this equation is dependent on the pore properties of the particles, and as long as the pore properties of the particles do not change, this correlation is expected to remain the same.

Using the effective diffusivity value and applying the shrinking core model (SCM), the rate at which the limestone solids would be converted under the experimental conditions with respect to time was estimated and the results are shown in Fig. 4.

The HF experiments were carried out as a continuous injection

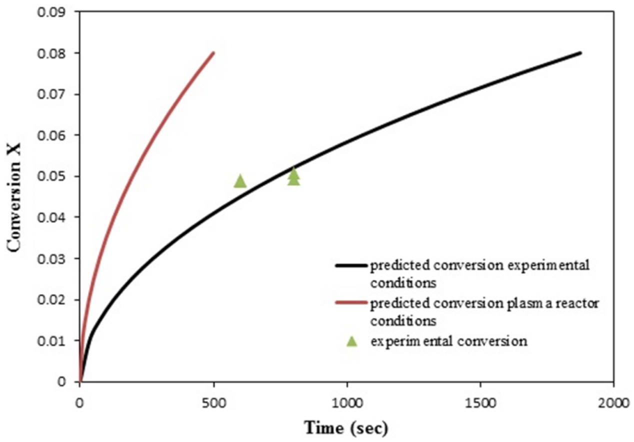

**Fig. 4. An estimation of the time it would take for the limestone particles with average particle radius 0.605 mm to be converted by the HCl gas at 408 K (experimental conditions) and 873 K (plasma reactor conditions).**

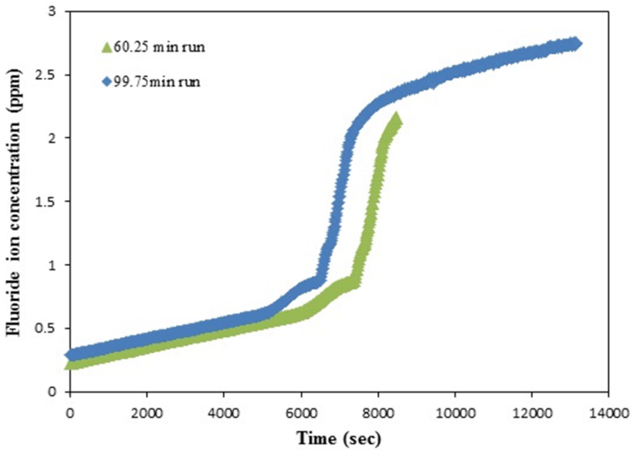

**Fig. 5. Typical breakthrough curves from the HF runs conducted at 60 and 99 minutes using the 0.584<R<0.625 mm particle size range.**

of 5% HF gas through the experimental system with the particle size range 0.584<R<0.625. The experiments ran for 60, 99 and 209 minutes. The results from a typical run of HF are shown in Fig. 5.

The amount of fluoride ions within the reacted solids from the reactor was estimated to be between 13.6% and 19.9% of the amount of calcium present within the limestone. It was observed that for the 60 minute run, the amount of HF gas that reacted with the limestone was greatest, followed by the 99 minute run, and finally the 209 minute run. This may be a result of the presence of a thicker product layer for the longer runs, which increases the time it takes for the gases to diffuse into the unreacted core resulting in slower reaction rates.

Based upon the amount of HF gas exiting the reactor, the amount of fluoride ions detected by the ISE, and the change in mass of the undissolved solids within the reservoir before and after the experiment, the fluoride ions that entered the reactor but were undetected by the ISE were assumed to be present as calcium fluoride in the reactor's solid media. This value, though lower than the measured final solid mass from the reservoir (as seen in Table 3), was close enough to the measured value to justify the lower fluoride ion concentration measured by the ISE. In addition, the relatively low solubility of calcium fluoride in water implies that the fluoride ions that reacted with the calcium ions present in the solution remained as calcium fluoride, thereby reducing the amount of free fluoride ions in solution measured by the ISE.

**Table 4. Estimated time for complete reaction of limestone particles with HF**

| | $D_e$ ($m^2$/s) | Time (hours) |
|---|---|---|
| Experimental $D_{e\ avg\ at\ 408\ K}$ | $2.20\times10^{-9}$ | 154.22 |
| Projected $D_{e\ avg\ at\ 873\ K}$ | $8.24\times10^{-9}$ | 41.20 |
| Theoretical $D_{e\ at\ 408\ K}$ | $4.12\times10^{-6}$ | 0.08 |

The amount of fluoride ions adsorbed in the reactor was compared to the expected amount using the change in mass of the reactor solids during the experiment. For simplicity, it was assumed that the initial mass of the solids was calcium carbonate and the final mass was a combination of calcium carbonate and calcium fluoride. The initial amount of calcium carbonate present was calculated as 0.0732 moles and the final calculated amount of calcium fluoride was 0.0088 moles; this resulted in a final calculated fluoride content of 0.0176 moles. This amount was higher than the value measured by the ISE, and may be attributed to the fact that not all the solid is present as calcium carbonate. In addition, there could have been some moisture content within the solids which was lost as a result of heating at 408 K.

From the HF run results, a similar linear scaling term was obtained. This suggests that there is a linear correction factor based on the internal properties of the solids. The effective gas diffusivities can be estimated at different temperatures from the product of the bulk diffusion of the gases and the linear correction factor. Therefore, once the internal properties of a solid particle are defined, the linear correction factor may be applied and a projection on the effective diffusivity of the gaseous substance into the solid at varying temperatures may be made. Table 4 compares the $D_e$ values from the different methods.

Considering that the effective diffusivity of the gas into the solids at higher temperature is much higher and the time for complete particle reaction is drastically reduced, it is probably because the temperature of the gases was increased, and thus the movement of the gaseous molecules into the solids increased correspondingly. Also, taking into account that the equation used to predict the diffusivities assumes a diffusion-limited process only, the neutralization reaction that occurs may be contributing to the variations in values observed.

**Table 3. Summary of the amount of HF adsorbed by limestone in the reactor and the neutralization reservoir**

| Time for runs (minutes) | 99.75 | 99.25 | 60.25 | 209.20 |
|---|---|---|---|---|
| Theoretical moles of HF fed based on flow rate and time (moles) | 0.09009 | 0.08962 | 0.05445 | 0.18582 |
| Fluoride ions adsorbed on limestone in reactor (moles) | 0.01330 | 0.01452 | 0.00991 | 0.01456 |
| HF exiting reactor into reservoir (moles) | 0.07679 | 0.07510 | 0.04454 | 0.17126 |
| Final measured Fluoride ion content in reservoir solution (moles) | 0.00037 | 0.00017 | 0.00002 | 0.01243 |
| Initial undissolved solids in reservoir (g) | 8.2586 | 8.2512 | 8.2525 | Not measured |
| Final undissolved solids in reservoir (g) | 6.9998 | 6.9906 | 6.9919 | Not measured |
| % of HF fed adsorbed by limestone | 14.77 | 16.20 | 18.19 | 7.84 |
| Initial mass of limestone particles in reactor | 7.3226 | 7.3253 | 7.3267 | 7.3236 |
| Final mass of limestone particles in reactor | Not measured | Not measured | Not measured | 7.1297 |
| % of limestone capacity in reactor used up | 17.34 | 19.86 | 13.55 | 19.92 |

**Table 5. The ratios of $D_e/D_{AB}$ at 408 and 873 K**

| Temperature (K) | Gas | $D_{AB}$ ($m^2/s$) | $D_e$ ($m^2/s$) | $D_e/D_{AB}$ (%) |
|---|---|---|---|---|
| 408 | HCl | $3.11\times10^{-5}$ | $1.50\times10^{-9}$ | 0.005 |
| | HF | $3.86\times10^{-5}$ | $2.20\times10^{-9}$ | 0.006 |
| 873 | HCl | $1.16\times10^{-4}$ | $5.560\times10^{-9}$ | 0.005 |
| | HF | $1.45\times10^{-4}$ | $8.20\times10^{-9}$ | 0.006 |

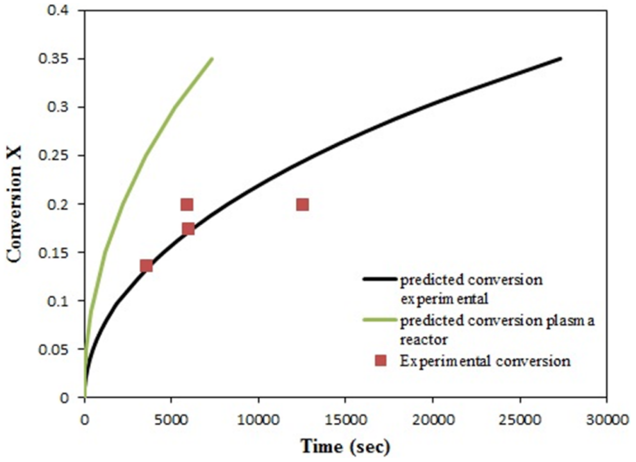

**Fig. 6. The estimated time at which the solid limestone particles with average particle radius 0.605 mm will be converted by the HF gases at 408 K (experimental conditions) and 873 K (plasma reactor conditions).**

To explain why a linear correction term may be applicable to this study, the effective diffusivity and bulk diffusivity of the gases at 408 K and 873 K were compiled and their ratios determined (Table 5). Solid conversion as a function of time was also determined, and is illustrated in Fig. 6. Considering the minimal difference between the $D_e/D_{AB}$ ratios, variations between the bulk and effective diffusivities were therefore assumed to be dependent on the internal properties of the solid particle, which reduced the diffusivity of the gas into the solid. Though there is a difference between the $D_e$ values obtained experimentally and those obtained theoretically, the theoretical effective diffusivity of HCl was lower than that of HF, and the same trend was observed from the experimental $D_e$ values. The ratio of the theoretical effective diffusivities to the experimentally obtained values for HF and HCl was found to be fairly consistent, suggesting that there is a linear correction factor based on the internal properties of the solid, which relates the diffusivity of the gases into the solid particle with the bulk diffusion of the gases into a porous medium. As the gases diffuse into the solid particles, depending on the diffusion mechanism in operation, it is expected that the diffusivity values would be less than what one would expect for a porous medium.

For illustrative purposes, previous studies on the effective diffusivity of nitrogen into solid materials at temperatures between 773 K and 1,023 K yielded diffusivities on the order of $10^{-15}$ $m^2/s$ [17]. This demonstrates the significantly lower diffusivity of gases into solid matrices.

For the purpose of evaluating the feasibility of an alternative adsorption media, one experiment was performed using a 50 wt% limestone, 50 wt% Portland cement powder. Of the 1.81% adsorbed, 1.16% was adsorbed by the limestone and 0.65% by the cement powder. Despite the fact that the reduced cement particle size (on the order of microns) should have resulted in a significant fraction of the HF being adsorbed into the cement matrix, the actual amount adsorbed was significantly lower than the amount adsorbed by the comparatively larger limestone particles. Given the difficulty associated with handling solid media within a process environment, the increased volume of cement which would be required relative to limestone (and potential issues with exceeding permissible fluoride levels) made this material unattractive as an adsorbent media.

Under the experimental conditions and using the $D_e$ values obtained, micron-sized particles would be required to obtain complete particle conversion times within seconds or minutes. This would require an entrained flow system where either dust handling infrastructure would be needed or the effluent stream would be injected into a water scrubber, effectively eliminating the intended advantages of a solid-phase neutralization system. Putting the results into perspective, the minimum amount of solid limestone required to neutralize the acidic gases generated from the destruction of ~12,000 kg of the refrigerant difluoromethane ($CH_2F_2$) at 873 K would be 7,400 kg. Using the Ergun equation, the required bed length and diameter needed to maintain a target pressure drop of 50,000 Pa was 12 m and 1.13 m, respectively. Considering the large vessel size required, the huge masses of solids required and the long particle reaction times, alternative processes need to be considered for HCl and HF gas neutralization after refrigerant breakdown.

## CONCLUSIONS AND RECOMMENDATION

In summary, this work explored the feasibility of solid media adsorption for the neutralization of effluent acidic gases from a plasma reactor destroying waste refrigerants. The solid media considered for this purpose were cement powder and limestone.

Cement powder was found to be an unattractive solid adsorbent because it requires large volumes to neutralize the acidic gases under the experimental conditions even as a powdery solid, adsorbed only 0.65% of fluorides when compared to 1.16% for limestone under the same conditions, and reduced the ability of the limestone particles to react with the HF gas. Limestone, however, was found to be a relatively suitable alternative, though under the experimental conditions it did not neutralize the acids to the extent that was expected.

The effective diffusivities of HCl and HF into the limestone particles under the experimental conditions were $1.5\times10^{-9}$ and $2.2\times10^{-9}$ $m^2/s$, respectively, and these values were used to estimate complete particle use times of 227 hours for HCl-limestone and 154 hours for HF-limestone under the experimental conditions. Furthermore, projected effective diffusivity values at plasma reactor temperatures reduced the particle consumption times to 61 hours and 41 hours for HCl and HF gases into limestone, respectively. These were obtained from effective diffusivity values of $5.61\times10^{-9}$ $m^2/s$ and $8.24\times10^{-9}$ $m^2/s$ at 873 K for HCl and HF in that order.

Considering the long particle consumption times observed for the 0.001 m diameter particles, there is the possibility of using smaller particle sizes (micron sized particles) to reduce these times into minutes or seconds. This would require entraining the particles in the gas flow for the neutralization to occur.

The relative ratios of the theoretical effective diffusivities for HF and HCl to the experimentally obtained values suggested that there is a linear correction factor based on the internal solid properties of the solid particle, which relates the bulk diffusion of the gases to the gas diffusivities within the solid particles. Therefore, once the internal properties of a solid particle were defined, the linear correction factor was applied and a projection on the effective diffusivity of the gaseous substance into the solid was made. Variations between the bulk and effective diffusivities were therefore dependent on the internal properties of the solid particle and these reduced the diffusivity of the gas into the solid.

Based on the results presented in this work, a liquid-based adsorption system to neutralize the acidic gases generated from the plasma reactor after waste refrigerant destruction is suggested. The potential to use solid-based systems may only be possible using smaller particle sizes, in which case the solids will have to be injected into the plasma reactor.

## LIST OF ABBREVIATIONS AND SYMBOLS USED

### Abbreviations

avg : average
CFO : critical flow orifice
ISE : ion selective electrode
SCM : shrinking core model
STP : standard temperature & pressure

### Symbols

b : stoichiometric coefficient of solid in chemical reaction
$C_{As}$ : bulk phase concentration of gas at particle surface
$D_{AB}$ : diffusion coefficient of gaseous mixture (HCl-nitrogen, HF-nitrogen)
$D_e$ : effective diffusivity
$M_{AB}$ : molecular mass of gas mixture (HCl-nitrogen, HF-nitrogen) in g/mol
P : pressure
$r_c$ : radius of unreacted core
R : initial radius of particle
t : time
T : temperature
wt% : weight percentage
X : conversion

### Greek Letters

$\rho_B$ : molar density of $CaCO_3$ in mol/m$^3$
$\sigma_A$ : Lennard-Jones length for HCl or HF
$\sigma_B$ : Lennard-Jones length for nitrogen
$\sigma_{AB}$ : characteristic length for HCl-nitrogen or HF-nitrogen
$\sigma_c$ : constriction factor
$\tau$ : tortuosity
$\phi_c$ : volume fraction of $CaCO_3$ in solid particle
$\phi_p$ : pellet porosity
$\Omega_D$ : dimensionless diffusion collision integral

## REFERENCES

1. O. Badr, S. D. Probert and P. W. O'Callaghan, *Appl. Energy*, **37**(4), 247 (1990).
2. J. C. Dickerman, *Technologies for CFC (Chlorofluorocarbons)/halon destruction*, Radian Corp.: Research Triangle Park, NC, USA (1989).
3. J. Heberlein, *Thermal plasmas for the destruction of hazardous wastes*, in *Conference proceedings - Italian Physical Society*, Editrice Compositori: Bologna, 18 (1994).
4. J. Heberlein and A. B. Murphy, *J. Phys. D: Appl. Phys.*, **41**(5), 053001 (2008).
5. T. Watanabe and S. Shimbara, *Halogenated Hydrocarbon Decomposition by Steam Thermal Plasmas*, ChemInform, **36**(25) (2005).
6. S. Yasui, T. Shojo, G. Inoue, K. Koike, A. Takeuchi and Y. Iwasa, *Int. J. Chem. Eng.*, **2012**, 1 (2012).
7. P. R. Jena, S. De and J. K. Basu, *Chem. Eng. J.*, **95**(1-3), 143 (2003).
8. S. Homma, S. Ogata, J. Koga and S. Matsumoto, *Chem. Eng. Sci.*, **60**(18), 4971 (2005).
9. K. Lee and O. Koon, *Chem. Eng. J.*, **146**(1), 57 (2009).
10. H. Y. Sohn and J. Szekely, *Chem. Eng. Sci.*, **27**(4), 763 (1972).
11. V. L. Hartmann, *Chem. Eng. J.*, **134**(1-3), 190 (2007).
12. S. Yagi and D. Kunii, *Symposium (International) on Combustion*, **5**(1), 231 (1955).
13. O. Levenspiel, *Chemical reaction engineering*, New York, Wiley (1999).
14. C. Y. Wen, *Ind. Eng. Chem.*, **60**(9), 34 (1968).
15. H. S. Fogler, *Elements of chemical reaction engineering*, Upper Saddle River, NJ, Prentice Hall PTR (2006).
16. B. E. Poling, J. M. Prausnitz and J. P. O'Connell, *The properties of gases and liquids*, New York, McGraw-Hill (2001).
17. C. R. Alpass, J. Murphya, A. Jainb and P. R. Wilshaw, *J. Electrochem. Soc.*, **156**(8), H669 (2009).