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ZERO-RELEASE MIXED WASTE PROCESS FACILITY DESIGN AND TESTING

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ABSTRACT

A zero-release offgas cleaning system for mixed-waste thermal treatment processes has been evaluated through experimental scoping tests and process modeling. The principles can possibly be adapted to a fluidized-bed calcination or stream reforming process, a waste melter, a rotary-kiln process, and possibly other waste treatment thermal processes.

The basic concept of a zero-release offgas cleaning system is to recycle the bulk of the offgas stream to the thermal treatment process. A slip stream is taken off the offgas recycle to separate and purge benign constituents that may build up in the gas, such as water vapor, argon, nitrogen, and CO_2. Contaminants are separated from the slip stream and returned to the thermal unit for eventual destruction or incorporation into the waste immobilization media.

In the current study, a standard packed-bed scrubber, followed by gas separation membranes, is proposed for removal of contaminants from the offgas recycle slipstream. The scrub solution is continuously regenerated by cooling and precipitating sulfate, nitrate, and other salts that reach a solubility limit in the scrub solution. Mercury is also separated by the scrubber. A miscible chemical oxidizing agent was shown to effectively oxidize mercury and also NO, thus increasing their removal efficiency.

The current study indicates that the proposed process is a viable option for reducing offgas emissions. Consideration of the proposed closed-system offgas cleaning loop is warranted when emissions limits are stringent, or when a reduction in the total gas emissions volume is desired. Although the current closed-loop appears to be technically feasible, economical considerations must be also be evaluated on a case-by-case basis.

INTRODUCTION

Under the Resource Conservation and Recovery Act (RCRA) and the Maximum Achievable Control Technology standards (MACT) for hazardous waste combustors, radioactive waste thermal treatment units have become increasingly more difficult to permit and operate. A new "zero-release" offgas control system has been developed for mixed-waste thermal treatment operations. The objective of the zero-release offgas system is to recycle hazardous constituents back to the waste treatment unit where they can be destroyed or bound and immobilized in the solid waste product. Nontoxic constituents that may build up in the offgas stream, such as water vapor, argon, nitrogen, and CO_2, are purged and safely discharged to the atmosphere.

The proposed development of a zero-release offgas control system for oxygen-blown hazardous waste incinerators was first proposed and published by Argonne National Laboratory in the early 1990's [1]. A new and unique zero-release configuration has been developed for possible implementation on mixed-waste treatment facilities. The New Waste Calcining Facility (Calciner) at the Idaho National Engineering and Environmental Laboratory (INEEL) was selected as an example study case.

The Calciner is a 1.5 meter diameter fluidized-bed of solid-waste particles (approximately 450 μm diameter on average) that are continuously generated by spraying a radioactive waste solution on the bed [2]. A kerosene-oxygen flame is used to heat the bed to around 773-873 K (500-600°C). As the bed height increases, the granular product is removed and transferred to a storage bin. The NWCF emits offgas with up to 3.5 vol.% NO_x (35,000 ppmv)[1] as a result of decomposition of the nitric acid and nitrate salts in the feed. Due to inefficient combustion of the kerosene, it emits 0.25-0.5 vol.% CO, plus unburned hydrocarbons. Table I summarizes the nominal NWCF exhaust gas composition.

Table I. INEEL New Waste Calciner Exhaust Gas Composition

Species	Nominal Concentration	Units
O_2	19.5	vol.%, dry
N_2	67.5	vol.%, dry
CO_2	9.0	vol.%, dry
CO	0.25-0.5	vol.%, dry
THC	250-1000	ppmv, dry
NO_2	2.5-3.0	vol.%, dry
NO	0.5-0.8	vol%, dry
NO_x	3.0-3.5	vol.%, dry
HNO_3	0-100	ppmv, dry
HCl	5-50	ppmv, dry
SO_2	0-5	ppmv, dry
H_2O	35	vol.%
Hg	5,000-25,000	μg/Nm^3, dry[b]
^3H	trace	(note a)
^{129}I	trace	(note a)

a. Emissions meet risk emissions levels for radionuclides
b. Nm^3 – standard cubic meters

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[1] ppmv – parts per million, volume basis ($1x10^{-6}$ [m^3 gas i]/[m^3 total gas])
vol.% - (100*[m^3 gas i]/[m^3 total gas])

The proposed zero-release configuration for the Calciner would recycle the offgas stream to the fluidize the bed as shown in Figure 1. This would allow CO_2 to build up in the offgas, when injecting only sufficient oxygen to burn the kerosene that is required to heat the bed. At steady-state, the dry offgas would consist mainly of CO_2 (>95 vol.%), 3-4 vol.% NO_x, 0.5-1vol.% CO, and <1 vol.% trace species. A slip stream would then be withdrawn to remove the CO_2 that builds up as well as any contaminants such as volatile mercury that accumulates in the gas stream. Nitrogen gas that enters the system by in-leakage into the sub-atmospheric process and also argon gas that naturally accompanies liquified oxygen would also be purged and released with the CO_2.

A basic scrubber would be used to remove scrubable species such as CO_2, HNO_3, NO_2, SO_2, HCl, and HF. Volatile metals, such as mercury compounds, and trace levels of radionuclides, would also be removed in the scrubber. An oxidizing agent would be required to convert elemental mercury to a scrubable mercuric salt. Unburned hydrocarbons which are not scrubbed from the offgas would be separated from the slip stream using standard membranes developed for natural gas cleanup. The unburned hydrocarbons would then be returned with the fluidizing gas recycle for destruction in the heated bed.

Scrub solutions would be regenerated by cooling and precipitating the nitrate, sulfate, and chloride salts that would accumulate in the scrub solutions. Conventional “freeze crystallization” technology could be used, if necessary, to precipitate and wash the salts and to remove any residual radioactive contamination prior to disposal of the salt sludge. Highly pure CO_2 could also be recovered for potential use as a plant seal or instrument purge gas. The excess CO_2 could be converted into solid or liquid product for sequestration or resale; although more likely, it would be released to the atmosphere as a non-pollutant.

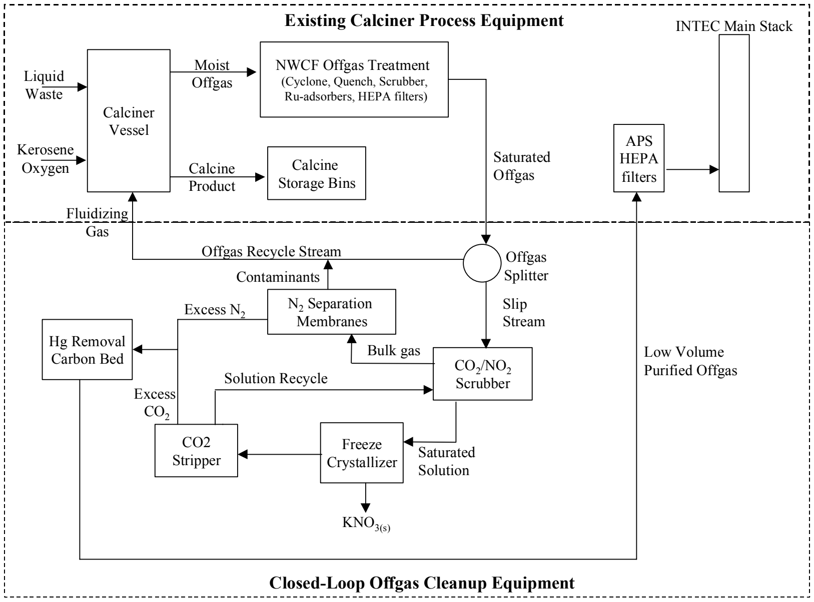

Figure 1. Proposed Calciner Closed-Loop Offgas Emissions System

In summary, the potential advantages of the closed-loop system for a candidate mixed waste treatment or chemical production process may include; multi-pollutant control (*e.g.* HCl, HNO_3, HF, NO_2, SO_2/SO_3, and oxidized mercury) in the caustic scrubber solution, recycle and destruction of unburned hydrocarbons, significantly lower volume of exhaust or stack gas discharged to the atmosphere, and attenuation of offgas transients associated with process upsets and/or variations in offgas composition.

Research Objectives and Approach

Laboratory testing of a carbonate scrubber column was completed to evaluate the technical feasibility of a closed-loop offgas treatment system on the NWCF. Although carbonate scrubbers were introduced over a century ago, there has been little to no operating experience at the conditions proposed for mixed-waste thermal treatment process offgas cleaning.
The main objective was to investigate the separation efficiency of CO_2, NO_2, SO_2, HCl, and mercury compounds.

A series of tests were conducted to measure CO_2, NO_2, NO, and SO_2 mass-transfer absorption coefficients, efficiency, and selectivity at sub-atmospheric pressure and as a function of carbonate solution strength and temperature for various CO_2-NO_2 offgas concentrations. The absorption efficiency of Hg^o (elemental mercury) vapor with a miscible oxidizing agent in a small scrubber was also tested to determine whether the removal of elemental mercury could be enhanced.

An equilibrium code for electrolyte solutions was used to model the solubility limits of dissolved nitrate/nitrite and sulfate/sulfite compounds in the carbonate-bicarbonate scrub solution. The results of these calculations provided indications on the feasibility and operating conditions for regeneration of the scrubber solution and the purity of the resultant precipitate.

Carbonate Scrubber Theory

Alkali carbonate solutions have the ability to absorb, by reaction, most of the common acid gases and CO_2. This property makes multi-contaminant removal feasible. Carbon dioxide reacts with the potassium carbonate to form bicarbonate, with NO_2 to form potassium nitrate, and with SO_2 to form potassium sulfite. In oxidizing conditions potassium sulfate will form. Halide gases react to form potassium halides. If Hg is oxidized, it will be scrubbed out as an insoluble mercuric carbonate or mercuric oxide. By adding an oxidizing agent to the solution, NO can be converted to NO_2 and elemental mercury (Hg^o) can be converted to mercuric oxide (HgO). The following equations sum the most important reactions relevant to the NWCF offgas.

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3 \qquad \text{(Eq.1)}$$

$$2K_2CO_3 + SO_2 + H_2O \leftrightarrow K_2SO3 + 2KHCO_3 \qquad \text{(Eq.2)}$$

$$2K_2CO_3 + 3NO_2 + H_2O \leftrightarrow 2KNO_3 + 2KHCO_3 + NO \qquad \text{(Eq.3)}$$

$$K_2CO_3 + HCl \leftrightarrow KCl + KHCO_3 \qquad \text{(Eq.4)}$$

$$NO + \text{Oxidant} \leftrightarrow H_2O + NO_2 \quad \text{followed by Eq. 3} \qquad \text{(Eq.5)}$$

$$Hg(g) + \text{Oxidant} \leftrightarrow HgO(s) + H_2O \qquad \text{(Eq.6)}$$

$$K_2SO_3 + \text{Oxidant} \leftrightarrow K_2SO_4 + H_2O \qquad \text{(Eq.7)}$$

Literature data [3] show better CO_2 removal at elevated temperature, increased K_2CO_3 concentration, and as expected, higher CO_2 partial pressure. The increased carbonate concentration and the increased temperature both increase the hydroxyl ion activity [4] and this has been shown to be the major influence factor on the absorption rate. As more CO_2 or acid gas is absorbed, the bicarbonate concentration increases, the pH decreases, and the rate of absorption falls. Design of any system would have to balance the absorption rate with scrub solution bicarbonate loading. All of the above potential gases, with the possible exception of mercury, contribute to this loading.

In order to increase gas loading in the scrubber solution, the carbonate concentration can be increased, but there are limits due to increased viscosity of the fluids. A 30 wt.% solution[2] was found to be about optimum for the tests performed in the packed-column setup for this study. At this concentration, all of the absorbed species remained dissolved in solution- even at 0°C - until the loading of nitrate or bicarbonate began to exceed the solubility limit. The viscosity of the scrub solution at this concentration did not result in column channeling.

The well-established Benfield process uses high pressure (about 20 bar) and relatively high temperature (about 400°K) to increase loading and can achieve a practical CO_2 loading of up to 2.1 mol/L. However, a high pressure driver is not suitable for mixed waste offgas systems. Radioactive processes are most typically operated at slightly sub-atmospheric conditions to prevent fugitive leaks of potentially radioactive gases and/or particulate.

Experimental Setup and Test Procedures

A small diameter "hood-compatible" laboratory scrubber was set up. The scrubber consists of a 25 mm internal diameter, 610 mm high, jacketed glass column (Figure 2). Physical characteristics of the packing were as follows:

- 4 mm Raschig rings, manually close-packed.
- a_t (total interfacial area per unit volume) of 1213 m^2/m^3
- a_{eff} (effective interfacial area, based on measurements) of 11.5 - 39 m^2/m^3

Tests were mainly conducted at two temperatures; 303 K or 323 K (30^{o}C or 50^{o}C). The temperature of the influent gas and scrub solution was controlled with a coolant that was chilled or heated in a constant temperature bath as shown in Figure 2. Liquid flow rates were in the range of 69-130 cm^3/min. The operating pressure was an average atmospheric pressure of 0.83 bar. Two scrubber liquors were tested- 0.8 and 2.8 mol/L potassium carbonate (K_2CO_3). The lower concentration is commensurate with earlier carbonate pilot plant scrubber tests [3, 4]. The higher concentration was required for the current application. Test gas mixtures were supplied by compressed gas cylinders. Gas flow rates were varied from 1.5 to 2.0 L/min at standard pressure and 294 K (21^{o}C). Target Hg^o concentrations were achieved by adjusting the bath temperature until the analyzer read the desired Hg^o concentration.

Carbon dioxide (CO_2) and sulfur dioxide (SO_2) were measured by infrared and electrochemical methods, respectively. Nitrogen dioxide (NO_2) and nitric oxide (NO) were measured with a chemiluminescent monitor. Elemental mercury (Hg^o) was measured with a PS Analytical Sir Gallahad semi-continuous analyzer calibrated by injection of measured diluted volumes of Hg^o

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[2] wt.% - (100*[kg compound i]/[kg solid])

vapor. Scrubber feed solutions and effluent samples were analyzed for carbonate (CO_3^{2-}), nitrate (NO_3^-), nitrite (NO^-), sulfate (SO_4^{2-}) and total sulfur.

In some of the tests, an oxidizing agent was either vaporized and added to the gas stream or added to the top of the scrubber in an attempt to enhance NO and Hg^o removal by oxidizing each species to NO_2 and HgO, respectively.

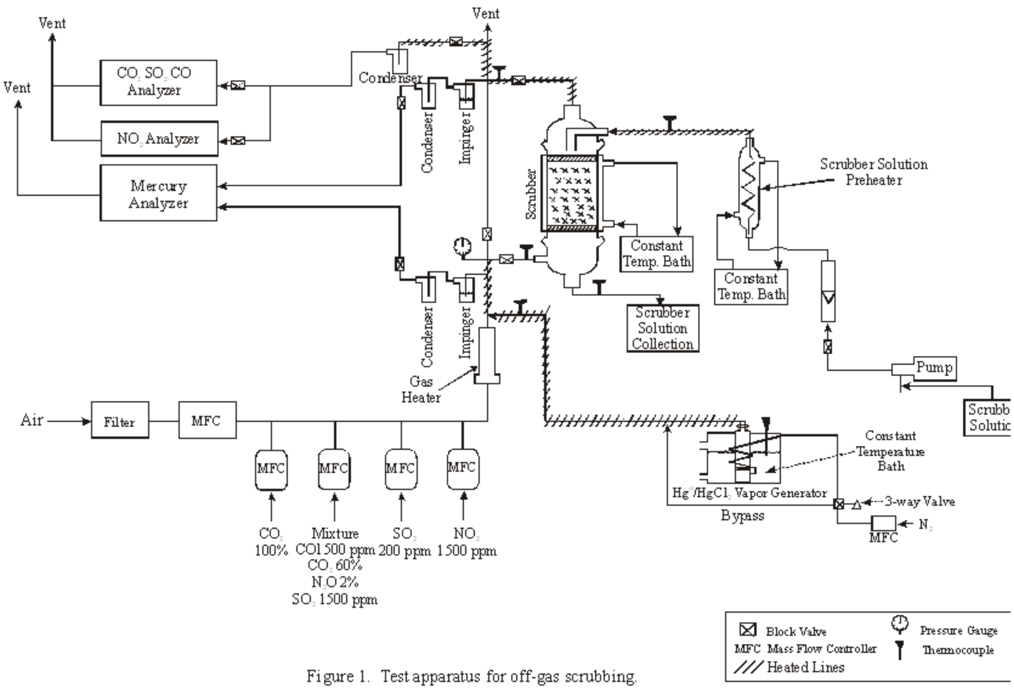

Figure 1. Test apparatus for off-gas scrubbing.

Figure 2. Experimental Packed-Column setup.

Experimental Results for Scrubbing Tests

The maximum demonstrated flows without flooding using water were found to be:

Gas $G = 4.7$ kg/hr·m^2
Liquid $L = 223$ kg/hr·m^2

Figure 3 plots test runs for the 0.8 mol/L carbonate solution. The results demonstrate a reasonable fit with the data from Comstock and Dodge [3]. The effective interfacial area was theoretically larger for the referenced data and the overall volumetric mass transfer coefficient should have been larger for the same conditions of temperature and pH.

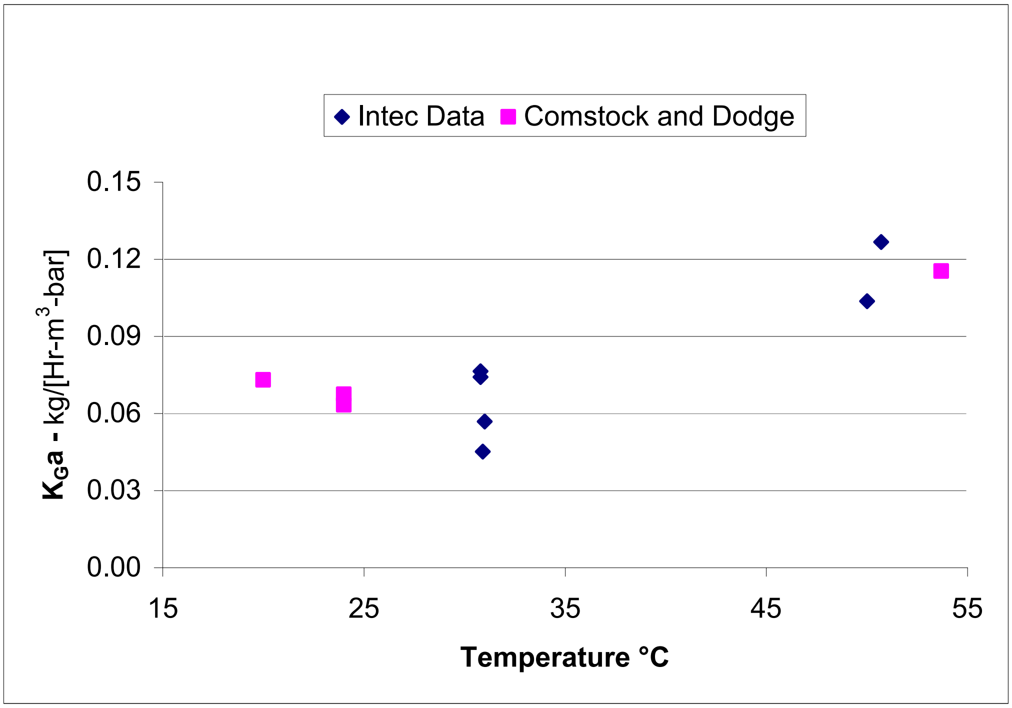

Figure 3. Comparison of experimental column performance with pilot scale results of Comstock and Dodge [3].

The results for the higher scrubber concentration (2.85 mol/L) are tabulated in Table II. The overall volumetric mass transfer coefficients, K_Ga's, determined for runs at 50° C and 2.8 mol/L are included in this table.

With the exception of Tests 11 and 12, the K_Ga's vary from about 0.12 to about 0.20 kg/(hr m^3 bar). Tests 1 and 2 had lower liquid flow rate than the balance of the runs, but it is not understood why Test 10 was lower than other runs at the same conditions. Test 10 also showed the poorest removal for NO_x.

Tests 5 and 6 were designed to test the removal of SO_2. The removal was near 100%. There was very little free O_2 in the feed gas because the SO_2 supply was 200 ppmv with N_2 as the diluent.

Analysis of the solutions showed no sulfate because there was very little oxidant. The dissolved specie was determined to be sulfite.

Table II. Summary of experimental scrubber results.*

Test #	Temp. °C	wt.% K_2CO_3 in solution	Inlet Liquid Molarity K_2CO_3	Percent CO_2 Removed	K_Ga kg/(hr-m^3-bar[CO_2])	Other Gases	Percent Removal of Other Gas
1	50.1	30.2	2.85	22.2	0.12	NO_2	56.13
2	50.1	30.3	2.86	24.2	0.13	NO_2	56.96
3	49.9	30.3	2.85	27.1	0.15	*NO*	12.13
4	50.3	30.3	2.85	22.1	0.15	NO_2	49.85
5	50.9	29.2	2.72	31.1	0.17	SO_2	98.08
6	50.8	28.5	2.65	30.9	0.16	SO_2	97.11
7	51.1	28.5	2.65			*Hg(g)*	2.70
8	50.1	27.2	2.50	24.4	0.13	*NO*	15.81
9	52	28.5	2.65	32.8	0.19	*NO*	10.31
10	52.7	28.7	2.67	21.5	0.12	*NO*	5.48
11	53.1	28.7	2.67	46.6	0.28	NO_2	40.80
12	52.5	28.7	2.67	50.8	0.32	NO_2 *Hg(g)*	66.51 88.0

* Inlet concentrations as follows: 40 vol.% CO_2, 1200 ppmv NO_2, 900 ppmv NO, 90 ppmv SO_2, 0.2 ppmv Hg^o

In the final two tests (11 and 12), an oxidizing agent was added to the scrub solution to enhance mercury oxidation and separation. A four-hour run, during which the average input Hg^o concentration was 1289 µg/m^3 (0.19 ppmv) measured at ambient conditions (28°C, 0.83 bar), resulted in 88% Hg^o removal. The scrubber and the Teflon tubing downstream of the scrubber were rinsed with 6 mol/L HNO_3 and the rinsate was analyzed for mercury. The results indicated that the total mercury trapped was nearly evenly distributed between the scrubber and the tubing. Since condensate was observed in the tubing during the test, oxidized mercury may have left the scrubber as an aerosol. It is also possible that about half of the mercury passed through the scrubber and was oxidized in the tube by the condensed oxidizing solution. The oxidizing agent also increased NO and NO_2 removal efficiency, presumably by reversing the reduction of NO_2 to NO in solution, and also by oxidizing gaseous NO to soluble NO_2.

Scrub Regeneration Thermodynamic Modeling Results

The dissolved salts in the scrub solution (mainly KNO_3, $KHCO_3$, and K_2SO_4) will build up in a scrubber solution recycle stream until their solubility limit is reached, or until they are removed by scrub regeneration. In order to regenerate the scrub solutions, either of the following unit operations may be viable; 1) steam stripping to regenerate K_2CO_3 from $KHCO_3$, and to concentrate the constituents (by removal of water) to their saturation limits where they would precipitate from solution, or 2) cooling the solution until the constituents reach their saturation limits and nucleate to form salt crystals that can be removed by filtration.

Based on these solution equilibrium dynamic predictions, it was shown that the best temperature to chill the slipstream to would be about 10°C since chilling would take more energy and would precipitate the sulfate monohydrate, K_2SO_4-H_2O, instead of K_2SO_4.

Conclusions and Recommendations

The proposed concept of a zero-emissions loops appear to be technically possible. The current study did not validate the economical nor regulatory advantages and disadvantages of the proposed option. Additional technical tradeoffs may also need to be considered.

Key technical findings of this study can be summarized as follows:

- Absorption of acid gases, such as CO_2, SO_2, and HCl, is highly effective in hot potassium carbonate scrub solutions, even at atmospheric pressure.
- Potassium carbonate was shown to be an effective solvent/scrubbing solution for CO_2 and NO_2. However, while NO_2 (nitrogen dioxide) is readily absorbed by the solution, approximately 50% undergoes reaction to form NO gas which is released back into the gas stream.
- In order to achieve a high NO_x removal efficiency (*viz.,* >50%), forced oxidation of NO to NO_2 or N_2O_5 is required.
- Absorption at near atmospheric pressure (*viz.,* 0.83 bar for these studies) can be accomplished with a reasonably sized column due to the relatively low volume of flow of the slip stream from the recycle gas loop.
- Speciated mercury will be effectively removed by the carbonate scrubber; however, oxidation of elemental mercury is required to achieve high removal efficiency for total mercury.
- A significant amount of $KHCO_{3(s)}$ will co-precipitate with $KNO_{3(s)}$ when the loaded scrub solution is chilled unless $CO_{2(g)}$ is first stripped from the scrub solution. This drives $KHCO_{3(soln)}$ to more soluble $K_2CO_{3(soln)}$.
- Following stripping of $CO_{2(g)}$, $KNO_{3(s)}$ and other salts near the solubility limit can be precipitated at around 10°C. Co-precipitation of some contaminates such as $Pb(NO_3)_{2(s)}$ and $HgCO_3$ will likely occur, necessitating second waste stabilization into a leach-resistant solid waste.
- All major pollutants can be removed with a high degree of efficiency, while reducing the volume of total offgas released to the atmosphere by over 90%. Benign constituent comprise the majority of the offgas release with only trace amounts of criteria pollutants being discharged.

Possible disadvantages and uncertainties of the proposed system design for mixed waste treatment applications may include, added offgas treatment equipment complexity, higher operating expense, and potential for excessive build-up of radionuclides in the scrubber solution requiring scrub solution recycle to the waste treatment process.

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