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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 CO₂. 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 CO₂, 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 ₂ O	35	vol.%
Hg	5,000-25,000	μg/Nm ³ , dry ^b
³ H	trace	(note a)
¹²⁹ I	trace	(note a)
a. Emissions meet risk emissions levels for radionuclides		
b. Nm ³ – standard cubic meters		

¹ ppmv – parts per million, volume basis (1×10^{-6} [m³ gas i]/[m³ total gas])
vol.% - ($100 \times$ [m³ gas i]/[m³ 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 CO₂ 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 CO₂ (>95 vol.%), 3-4 vol.% NO_x, 0.5-1 vol.% CO, and <1 vol.% trace species. A slip stream would then be withdrawn to remove the CO₂ 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 CO₂.

A basic scrubber would be used to remove scrubable species such as CO₂, HNO₃, NO₂, SO₂, 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 CO₂ could also be recovered for potential use as a plant seal or instrument purge gas. The excess CO₂ 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.

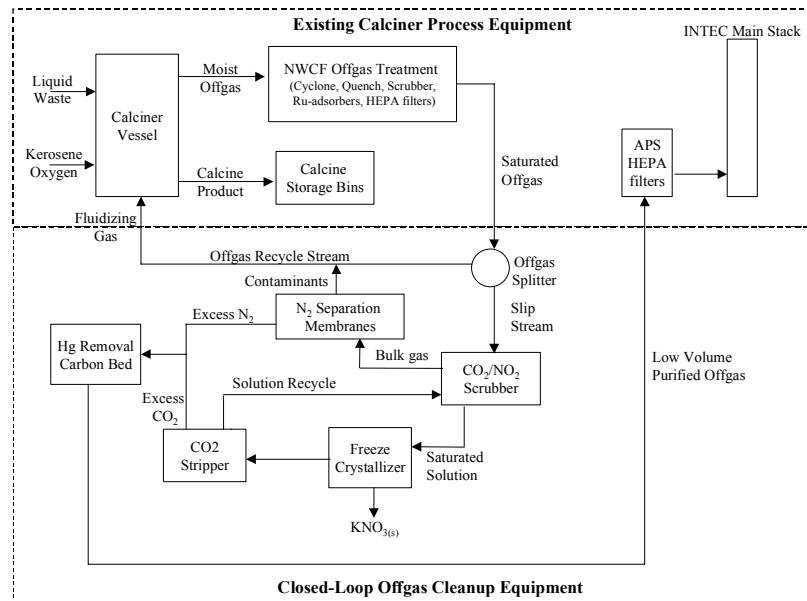


Figure 1. Proposed Calciner Closed-Loop Offgas Emissions System

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, HNO₃, HF, NO₂, SO₂/SO₃, 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 CO₂, NO₂, SO₂, HCl, and mercury compounds.

A series of tests were conducted to measure CO₂, NO₂, NO, and SO₂ mass-transfer absorption coefficients, efficiency, and selectivity at sub-atmospheric pressure and as a function of carbonate solution strength and temperature for various CO₂-NO₂ offgas concentrations. The absorption efficiency of Hg⁰ (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 CO₂. This property makes multi-contaminant removal feasible. Carbon dioxide reacts with the potassium carbonate to form bicarbonate, with NO₂ to form potassium nitrate, and with SO₂ 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 NO₂ and elemental mercury (Hg⁰) can be converted to mercuric oxide (HgO). The following equations sum the most important reactions relevant to the NWCF offgas.



Literature data [3] show better CO₂ removal at elevated temperature, increased K₂CO₃ concentration, and as expected, higher CO₂ 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 CO₂ 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.% solution² 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 CO₂ 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 m²/m³
- a_{eff} (effective interfacial area, based on measurements) of 11.5 - 39 m²/m³

Tests were mainly conducted at two temperatures; 303 K or 323 K (30°C or 50°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 cm³/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 (K₂CO₃). 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°C). Target Hg⁰ concentrations were achieved by adjusting the bath temperature until the analyzer read the desired Hg⁰ concentration.

Carbon dioxide (CO₂) and sulfur dioxide (SO₂) were measured by infrared and electrochemical methods, respectively. Nitrogen dioxide (NO₂) and nitric oxide (NO) were measured with a chemiluminescent monitor. Elemental mercury (Hg⁰) was measured with a PS Analytical Sir Gallahad semi-continuous analyzer calibrated by injection of measured diluted volumes of Hg⁰

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_2^-), 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^0 removal by oxidizing each species to NO_2 and HgO , respectively.

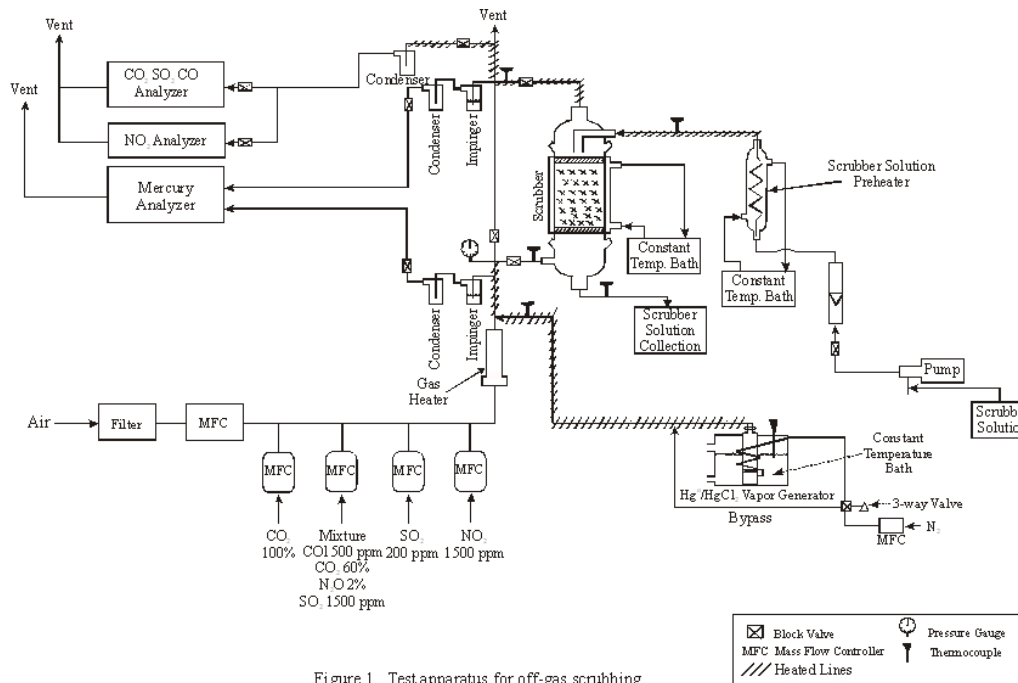


Figure 1. Test apparatus for off-gas scrubbing

Figure 2. Experimental Packed-Column setup.

Experimental Results for Scrubbing Tests

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

$$\begin{aligned} \text{Gas } G &= 4.7 \text{ kg/hr}\cdot\text{m}^2 \\ \text{Liquid } L &= 223 \text{ kg/hr}\cdot\text{m}^2 \end{aligned}$$

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.

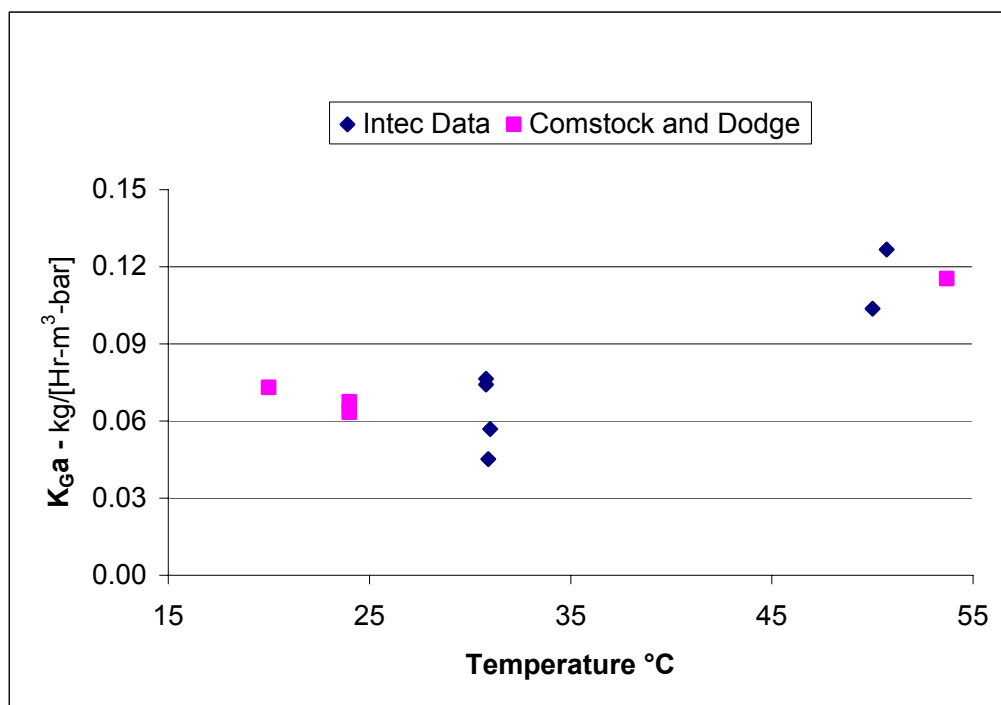


Figure 3. Comparison of experimental column performance with pilot scale results of Comstock and Dodge [3].

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 m³ 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 SO₂. The removal was near 100%. There was very little free O₂ in the feed gas because the SO₂ supply was 200 ppmv with N₂ 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 ₂ CO ₃ in solution	Inlet Liquid Molarity K ₂ CO 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.% CO₂, 1200 ppmv NO₂, 900 ppmv NO, 90 ppmv SO₂, 0.2 ppmv Hg⁰

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 Hg⁰ concentration was 1289 µg/m³ (0.19 ppmv) measured at ambient conditions (28°C, 0.83 bar), resulted in 88% Hg⁰ removal. The scrubber and the Teflon tubing downstream of the scrubber were rinsed with 6 mol/L HNO₃ 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 NO₂ removal efficiency, presumably by reversing the reduction of NO₂ to NO in solution, and also by oxidizing gaseous NO to soluble NO₂.

Scrub Regeneration Thermodynamic Modeling Results

The dissolved salts in the scrub solution (mainly KNO₃, KHCO₃, and K₂SO₄) 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 K₂CO₃ from KHCO₃, 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, K₂SO₄·H₂O, instead of K₂SO₄.

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 $\text{KHCO}_{3(\text{s})}$ will co-precipitate with $\text{KNO}_{3(\text{s})}$ when the loaded scrub solution is chilled unless $\text{CO}_{2(\text{g})}$ is first stripped from the scrub solution. This drives $\text{KHCO}_{3(\text{soln})}$ to more soluble $\text{K}_2\text{CO}_{3(\text{soln})}$.
- Following stripping of $\text{CO}_{2(\text{g})}$, $\text{KNO}_{3(\text{s})}$ and other salts near the solubility limit can be precipitated at around 10°C . Co-precipitation of some contaminants such as $\text{Pb}(\text{NO}_3)_2$ 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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