

Dry-Packed Beds for the Removal of Strong-Acid Gases From Recycled Atmospheres

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ABSTRACT

Under certain conditions, strong-acid gases can be formed in recycled atmospheres by the combustion of halogenated hydrocarbons. One control measure involves the use of a dry absorbent filter. Li_2CO_3 has already been used as an absorbent in these filters as a result of a screening test of a number of scavenger materials. In this report the absorptive properties of some other potentially useful materials were examined. Baralyme and soda lime were superior to Li_2CO_3 in air at 76°F and over 50% R.H., while the silica-alumina catalyst with monoethanolamine (MEA) impregnant and the silica-magnesia catalyst were almost as effective as Li_2CO_3 . However, Baralyme, soda lime, various basic materials (MEA, gaseous NH_3 , Na_2CO_3 , and quinoline) supported on the silica-alumina catalyst, and the silica-magnesia catalyst were all useless at 140°F, especially under dry conditions. Li_2CO_3 , therefore, still remains as the most effective absorbent throughout the range of probable conditions.

PROBLEM STATUS

This is a final report on this phase of the problem.

AUTHORIZATION

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DRY-PACKED BEDS FOR THE REMOVAL OF STRONG-ACID GASES FROM RECYCLED ATMOSPHERES

INTRODUCTION

Under certain conditions, strong-acid gases can be formed in closed atmospheres by the combustion of halogenated hydrocarbons. One control measure involves the use of a dry absorbent filter. Restrictive flow conditions caused by space limitations in recycled atmospheres impose a stringent requirement on any absorbent, because the pressure drop across such a filter would have to be less than 1 in. H_2O .

Materials considered for removing strong-acid gases from closed atmospheres by a fixed absorbent bed have been reported previously. Additional potentially useful materials were subsequently tested, and the results of these tests are given in this report. Among these materials are the CO_2 absorbents, Baralyme and soda lime. Other possibilities tested are porous catalysts with large surface area per unit weight, which could react either independently (silica-magnesia) or by virtue of available surface acidic sites (silica-alumina). Such acidic sites could easily be converted to basic sites by either liquid or vapor phase impregnation with basic substances.

METHOD OF TESTING

A 2-in. bed of the test material was supported by a stainless steel screen in a 2-in.-diameter acrylic resin assembly. Ambient air flowing at 0.92 cu ft/min and having the desired humidity was mixed with the test gas, which was selected to be HCl. For the high-temperature tests, the air was heated before being mixed with the gas. To accelerate the tests, a flow of 0.65 cc/min of anhydrous HCl from a lecture bottle was used, and this resulted in an influent concentration of 25 ppm HCl. The concentration was confirmed by absorption of the gas in known excess of 0.1N NaOH and subsequent titration with 0.1N H_2SO_4 to determine the amount of NaOH neutralized. The contaminated air was then passed down through the filter.

BARALYME TESTS

The Baralyme used in these tests contained 20% $Ba(OH)_2 \cdot 8H_2O$ and 80% $Ca(OH)_2$. Inert material and free H_2O were not present.

A 2-in.-thick filter at room temperature with humid air, over 50% R.H., removed 8.3 g HCl. Although no HCl was detected in the effluent air, the test was terminated with the appearance of liquid drippings which result in unpredictable pressure drops. The average concentration of HCl during this test was 19 ppm. It was calculated that with a 25-ppm HCl input, the Baralyme would have been effective for 131 hours.

In another test a 4-in.-thick filter of Baralyme was used at 140° F. This filter's performance was affected drastically by the moisture content of the air. Practically all of the HCl passed through the filter at a partial pressure of H_2O of 8 mm Hg or less, but when the partial pressure was increased to 19 mm Hg, all of the HCl was absorbed. Since a sudden increase in humidity could briefly lower the concentration of HCl, the HCl input to the filter was verified at 25 ppm at the H_2O partial pressure of 19 mm Hg. However, even with

this high moisture content (80% R.H. at 76°F), 3 to 6 ppm HCl were found in the effluent air after 47 hr. By comparison, a Li_2CO_3 filter of half the thickness was effective more than twice as long.

SODA-LIME TESTS

A 2-in. filter of soda lime, nominally 80% $\text{Ca}(\text{OH})_2$, 4% NaOH, 15% H_2O , and 1% inert binder, also performed effectively under humid conditions at room temperature. After 108 hours the soda lime absorbed 6.9 g HCl from air containing 25 ppm HCl. The test was concluded when enough deliquescence had occurred to produce liquid drippings.

In another test at 140°F the same thickness of soda lime failed rather quickly, although its use could be prolonged by an increase in the moisture content of the air. With a partial pressure of H_2O of 8 mm Hg or less, the soda lime allowed about 3 ppm HCl to pass through the filter after 19 hr of service. The usefulness of this filter could then be extended by increasing the moisture content of the air. Breakthrough times at higher partial pressures of H_2O were roughly 28 hr at 12 mm Hg and 50 hr at 14 mm Hg.

SILICA-ALUMINA-CATALYST TESTS

Pelleted silica-alumina catalyst, Grade 980, a product of Davison Chemical Company, is available in either 1/8 by 1/8 in. or 3/16 by 3/16 in. cylindrical pellets, each in two different chemical compositions. The chemical and physical analyses supplied by Davison are as follows:

"13% Alumina"

SiO_2 , 87 wt-%	Bulk density, 39 lb/cu ft
Al_2O_3 , 13 wt-%	Surface area, 500 m^2/g
Na_2O , 0.02 wt-%	Pore volume, 0.75 cc/g
Fe_2O_3 , 0.05 wt-%	Av pore diameter, 60 Å

"25% Alumina"

SiO_2 , 75 wt-%	Bulk density, 39 lb/cu ft
Al_2O_3 , 25 wt-%	Surface area, 400 m^2/g
Na_2O , 0.04 wt-%	Pore volume, 0.70 cc/g
Fe_2O_3 , 0.05 wt-%	Av pore diameter, 70 Å

The 1/8 by 1/8 in. pellets were used in the tests. For either vapor or liquid phase impregnation, the treatment consisted of evacuation with a water aspirator and slow addition of the impregnant to the pellets. The pellets were then dried externally, if required, while some of the liquid was retained by the interior pores.

Monoethanolamine (MEA) Impregnant

With aqueous 6N monoethanolamine (MEA) solution as impregnant, a 2-in. filter of 13% alumina absorbed 8.5 g HCl, as determined by chemical analysis. This amounts to the total removal of HCl for 132 hr under test conditions and at room temperature. Throughout the test, the appearance of a yellow-orange band, probably hygroscopic $\text{MEA}\cdot\text{HCl}$, indicated progress of absorption. The effluent air from the filter was alkaline during the time of total removal of HCl. Air samples taken with MEA and NH_3 detector tubes (1) revealed that at room temperature the pellets evolved 1 ppm NH_3 or less but no MEA in both the presence and absence of HCl in the influent air. Near the end of the test, at a time corresponding to the absorption of 6.6 g HCl, some NH_4Cl (but no HCl) was evident in the

effluent tube. The appearance of NH_4Cl , another corrosive substance, can also be considered a breakpoint. At the end of the test, the effluent air was neutral.

In another test, fresh pellets were impregnated with MEA solution; but this time the MEA was carbonated and the filter temperature was increased to 140°F . The effluent air was again alkaline; but now not more than 0.5 ppm MEA was detected, and no NH_3 was found. However, in less than 29 hr, NH_4Cl and 3 ppm HCl were found in the effluent air. At room temperature, this filter removed all HCl for the next 10 hr. When the filter temperature was again increased to 140°F , 1 ppm HCl was found in the effluent air in less than 3 hr. This pattern of HCl breaking through at 140°F but being removed at room temperature was repeated in additional tests. Finally, after 45 hr, the air downstream from the filter at room temperature gave a neutral reaction. At this time, operation at 140°F resulted in a more pronounced breakthrough, as 3 to 4 ppm HCl appeared in the effluent air within 1/2 hr. During this test, it was determined that HCl would not be evolved from the partially used filter by merely heating air without HCl to 140°F . As might be expected, the use of 25% alumina with a smaller surface area did not result in any improvement.

Other Impregnants

Other impregnants, such as gaseous NH_3 , a saturated aqueous solution of Na_2CO_3 , and quinoline, were tried at 140°F , and each was found unsatisfactory. Tests at room temperature were omitted. Using NH_3 impregnant, breakthrough occurred suddenly and decisively, as 15 ppm HCl were found in the effluent air in less than 5 hr. Using Na_2CO_3 , a breakthrough of about 1 ppm HCl was evident in 20 hr, and with quinoline an objectionable odor precluded further evaluation. Although quinoline is not particularly unpleasant at room temperature, it becomes disagreeable in time. It is definitely obnoxious at 140°F , even though it has the relatively high boiling point of 459°F .

SILICA-MAGNESIA-CATALYST TESTS

Silica-magnesia catalyst in the form of 3/16 by 3/16 in. cylinders was also obtained from the Davison Chemical Company. Supplied analyses indicate 30% MgO and 70% SiO_2 on a dry basis, an extruded-form bulk density of 42 lb/cu ft, a surface area of $500\text{ m}^2/\text{g}$, and a pore volume of 0.65 cc/g. These pellets were not impregnated, but they were exposed overnight to a 100% CO_2 atmosphere. The weight of CO_2 absorbed was negligible.

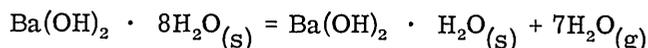
This catalyst has about half the ultimate capacity for HCl as an equal volume of Li_2CO_3 . However, HCl breaks through after about 10% conversion of the Li_2CO_3 ; this may indicate a surface reaction that isolates the interior of the Li_2CO_3 . Therefore, it was still possible for the catalyst to be as effective as or perhaps better than Li_2CO_3 , depending on how effectively its capacity could be used.

At room temperature, a 2-in. filter allowed very low concentrations of HCl to pass through practically throughout the test. An increase in the moisture content of the air reduced these concentrations to virtually nothing; for instance, 0.6 ppm HCl was lowered to 0.2 ppm by merely increasing the partial pressure of H_2O from 11 to 14 mm Hg. After 107 hr, 2.0 to 2.5 ppm HCl were found in the effluent air, but by this time the filter had absorbed 6.6 g HCl. Under the same conditions, a Li_2CO_3 filter would have the advantage in that HCl removal would be complete for almost the same period. However, techniques for rapid detection of very low concentrations of HCl (2) had not been developed at the time the Li_2CO_3 filter was tested.

At 140°F , the silica-magnesia filter failed at the start, even with a relatively high moisture content (a partial pressure of H_2O of 18 mm Hg), as 2 to 3 ppm HCl were detected in the effluent air in 2 to 3 hr.

DISCUSSION

Unlike Li_2CO_3 , which can absorb HCl over a wide range of moisture conditions, the substances reported herein function poorly under dry conditions. The differences in HCl absorption by Baralyme and soda lime, although the two are somewhat similar in that both have a high $\text{Ca}(\text{OH})_2$ content, may well be caused by a difference in availability of moisture. Soda lime, with 14 to 19% free water, has an advantage over Baralyme, which has water of crystallization. Both will lose most of their water in a hot, dry atmosphere; however, the loss of water from Baralyme is somewhat unique, since the decomposition pressure for the reaction

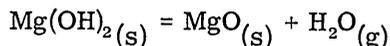


is about 60 mm Hg (0.079 atm) at 331°K (from International Critical Tables). This reaction could cause a very rapid loss of water.

For the silica-alumina catalyst, with a diameter of 2 in. and a thickness of 2 in. and the weights of the pellets before and after impregnation, it was determined that 28 g, and therefore 28 cc, of MEA solution had been retained. The available pore volume, however, was 47 cc, as calculated from filter dimensions, pellet density, and pore volume per unit weight. No further attempts were made to increase the amount of MEA solution retained by the catalyst because of the undesirable evolution of NH_3 and MEA gases. The 28 cc of MEA solution, containing 10.3 g MEA, can react with 6.1 g HCl. The additional 2.4 g HCl absorbed in the test at room temperature would then have to be absorbed by the solvent, 18 cc H_2O , since physical adsorption by silica-alumina itself would be negligible. At 25 ppm HCl, the partial pressure of HCl would be 0.019 mm Hg. Consequently, about 13 g HCl could dissolve per 100 g H_2O . The 18 cc H_2O could therefore dissolve about 2.3 g HCl. Thus, a complete reaction with MEA, as well as saturation of H_2O by HCl, seems to have been verified. In this instance, the effectiveness of the absorbent throughout its consumption is somewhat remarkable.

Unfortunately, the MEA-impregnated catalyst became useless at 140°F, apparently because of rapid loss of water by evaporation. The psychrometric chart shows that air heated from 76°F and 50% R.H. to 140°F will have its R.H. reduced to 8%. This dry air flowing at about 1 cu ft/min can easily remove the small amount of H_2O involved in a matter of hours.

In the case of silica-magnesia catalyst, the difference in performance with temperature suggests that a reaction of magnesia with H_2O to form $\text{Mg}(\text{OH})_2$ is a prerequisite to the absorption of HCl. According to the International Critical Tables, the decomposition pressure for the reaction



is about 49 mm Hg (0.064 atm) at 144°F. Another source (3a) verifies this result with the following data for the H_2O -vapor pressure (mm Hg): 1.75 at 77°F, 31.5 at 127°F, and 92.0 at 165°F. Thus, $\text{Mg}(\text{OH})_2$ is stable at room temperature, but is not stable in dry air at 140°F. Another reason for not operating a magnesia filter at higher temperatures is that $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ will begin to evolve HCl at 223°F, according to R. Brandes (3b).

CONCLUSIONS

Li_2CO_3 absorbs strong-acid gases over a greater range of temperatures, and possibly at lower humidities, than all the materials tested. Baralyme was the best absorbent, while soda lime ranked slightly ahead of Li_2CO_3 in air at 76°F and over 50% R.H. Under the same conditions, silica-alumina catalyst with MEA impregnant and silica-magnesia catalyst were

almost as effective as Li_2CO_3 , but the MEA-impregnated catalyst continuously evolved 1 ppm NH_3 or less, and the silica-magnesia allowed traces of strong-acid gas to pass through the filter throughout the test. Since an appreciable quantity of absorbent would be required, Baralyme could be considered a toxic hazard. The effectiveness of soda lime under dry conditions at room temperature is believed to be reduced, but was not determined since possible operation at higher temperatures would result in an early breakthrough of the strong-acid gas. In fact, all of the absorbents, except Li_2CO_3 quickly failed at an operating temperature of 140°F. Thus, at this time, Li_2CO_3 is still recommended as the most effective absorbent for strong-acid gases in a closed atmosphere.

REFERENCES

1. Williams, D.D., and Smith, S.H., Jr., "The Determination of Microgram Quantities of Monoethanolamine and Ammonia in Air," NRL Memo. Rept. 898, Jan. 1959
2. Williams, D.D., Johnson, E.T., and Miller, R.R., "A Method for the Determination of Strong-Acid Vapors in the PPM Range," NRL Rept. 6332, Oct. 1965
3. Mellor, J.W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, Green and Co., 1957
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