

APPLICATION OF THE SODIUM
DUAL ALKALI SCRUBBING PROCESS
TO HIGH CHLORIDE GAS STREAMS

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INTRODUCTION

The methods used for disposing of military chemical agents, such as VX, GB, and H, have been changed from land and sea burial to chemical neutralization and incineration due to environmental constraints and legislative restrictions.

As an approach to munitions disposal, the Army has developed a Chemical Agent Munitions Disposal System (CAMDS) facility at the Tooele Army Depot, Tooele, Utah. This is a prototype for other lethal chemical demilitarization plants expected to be built in the future.

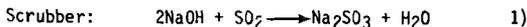
The CAMDS facility was especially designed for the safe handling, disassembly, destruction, and decontamination of chemical agents VX, GB, and H, and munitions containing these chemical agents. These disposal operations must include adequate emission control technology. The emissions of concern include not only the agents themselves, but also certain species produced in the disposal process, such as sulfur oxides (SO₂ and SO₃), phosphorus oxides (e.g., P₂O₅), hydrogen chloride (HCl), and particulate matter.

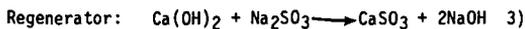
Although the present method of gas treatment is believed to have excellent reliability, it is costly to operate because of its raw material requirements and its material handling procedures. A particularly expensive step in the overall gas treatment procedure is the required evaporative drying of salts which results from the use of the CAMDS single alkali scrubbing system. Alternatives to the evaporative drying of the salts have been investigated in order to reduce the energy consumption of the facility.

After demilitarization of a munition at the CAMDS facility, the metal parts are conveyed into the metal parts furnace (MPF), a roller hearth furnace, where residual agent on metal parts is thermally destroyed. Bulk mustard is also destroyed in the MPF. Exhaust from this furnace is treated in an extensive control system comprising (a) an oxidizing section for thermally decomposing any residual agents at 1600 F, (b) a quench venturi, and (c) a packed column where the exhaust gases are contacted with NaOH or Na₂CO₃ solution. Exhaust from the packed tower exits through a stack to the atmosphere.

To avoid buildup of phosphates, sulfates, and chlorides in the scrubber solution, a portion of the scrubber stream is removed from the system and evaporated to dryness. The resultant dry salts are then placed in drums for storage. The evaporation step requires large amounts of energy. The use of dual alkali scrubbing technology could avoid the need to evaporate large amounts of water to produce a solid waste.

In the sodium-based dual alkali process, the acid gases are absorbed by a solution of sodium salts at a pH range of 5-8. The solution is regenerated outside the scrubber with lime or limestone to produce a solid waste containing calcium sulfate and calcium sulfite. Some sodium salts are lost with the waste and must be made up by the addition of NaOH or Na₂CO₃. The principal chemical reactions are as follows:





One consideration in specifying a dual alkali system for the MPF is the relatively high concentration of HCl in the flue gas during mustard operations. The NaCl resulting from the reaction of NaOH and HCl cannot be regenerated with Ca(OH)₂ and must be purged from the system. In order to avoid a liquid purge stream which would have to be dried, the process in Figure 1 was designed to remove the NaCl with the liquid in the filter cake.

Dual alkali systems have been extensively applied to scrubbing SO₂ from boiler flue gas. In most of these applications, the objective in using a dual alkali system as compared to a single alkali system, is to minimize the use of the more expensive sodium as compared to the calcium in lime. However, the most cost-effective operation for the system on the MPF is one that will eliminate the expensive drying process. The design shown in Figure 1 may actually require considerably more alkali than the minimum required in order to increase the solids content in the waste filter cake and thereby allow the NaCl to be purged with the liquid attached to the filter cake. In order to minimize this quantity of liquid, the chloride content is allowed to build up to very high levels.

The principal advantage of a dual alkali process applied to the MPF is the substitution of a relatively inexpensive filtering step for the expensive drying step in the single alkali system.

RESULTS AND DISCUSSION

After assembling the sodium dual alkali pilot plant shown in Figure 1, it was operated at several different conditions to explore the scrubbing efficiency, the effect of chloride buildup in the scrubbing liquor, and to obtain a material balance. Tables 1A and 1B summarize the data obtained in the 13 runs made in the pilot plant.

Scrubbing Efficiency

The effect of the stoichiometric ratio of total alkali [Ca(OH)₂ plus NaOH] to total acid gas (SO₂ plus HCl) is shown in Figure 2. The theoretical limit for reaction of the alkali with the acid gases is indicated in the figure. (Actually, some removal of HCl can be expected with no alkali present.) Sulfur dioxide removal efficiencies were found to exceed 99 percent when alkali/acid stoichiometric ratios were greater than about 1.9. HCl removal efficiencies generally exceed SO₂ removal at any given alkali/acid stoichiometric ratio.

Effect of Chloride Buildup

Removal Efficiency. The outlet stream from the regeneration tanks was filtered to remove the solids. A typical filtrate composition at the higher chloride concentration range is presented in Table 2. The filtrate was recycled to the system, mixed with additional sodium hydroxide, and pumped back into the column as scrubbing liquor. Chloride built up as the scrubbing reaction occurred.

Figure 3 shows percent SO₂ remaining in the scrubbed gas as a function of alkali/acid gas stoichiometric ratio. The numbers beside each point are chloride concentration in the scrubber liquor. From an examination of this figure, it does not appear that chloride concentration has any significant effect on SO₂ removal in the range studied.

Solids Precipitation. Although chloride concentration in the scrubber liquor has little effect on removal efficiency, it has a significant effect on the operation of the column. Chloride concentrations greater than about 6.6 percent (see Table 3), lead to some deposit of salts in the scrubber column. Nevertheless, it appears that if chloride level is maintained below about 8-1/2 to 9 percent, column operation

would not be impaired. Figure 4 shows chloride concentration of the last nine runs together with an indication of the degree of column plugging.

Precipitation occurs when solubility limits of the components in solution are exceeded. This is the case when Cl^- concentration in the scrubbing liquor reaches values above 6.6 percent. These salts redissolve in the liquor, indicating that they are most likely sodium salts.

Chloride is removed with the moisture in the cake, thus maintaining a steady-state concentration. Essentially no chloride is removed as a solid as shown in a typical dry cake analysis (Table 4).

The other type of salt precipitating in the column is calcium-based. Elimination or reduction of calcium ions in the liquor is critical if the temperature in the system drops. A larger amount of precipitate was observed in the pilot plant when overnight temperature dropped to about 60 F. Most of these salts returned to solution after the system was reheated to operating temperatures. This relationship between the temperature and precipitation must be taken into consideration in the design and operation of a full-scale plant. As indicated by the analysis and postulated composition shown in Table 5, these salts are believed to be primarily calcium sulfite and sulfate.

Operation of a dual alkali plant would be significantly impaired if precipitation is allowed in the system. For example, as observed during pilot plant operation, precipitation present at the nozzle and in the column sometimes limited the amount of liquor input to the column.

Tower and packing designs also affect the accumulation of insoluble matter in the column. A spray tower design would considerably reduce the plugging potential, but at the expense of scrubbing efficiency. The packing size, shape, and height are also critical to the plugging problem. Large size, open shape, and low packing height would all minimize plugging. However, the large size has a reduced surface area per unit volume which may cause a reduction in scrubbing efficiency. The low packing height would also reduce the scrubbing efficiency. During the pilot plant operation, no attempt was made to optimize the packing material.

The area of scrubber plugging has been the subject of intense study by investigators of conventional limestone and dual alkali scrubbing systems.

Material Balance

In Pilot Plant Run No. 10, all the materials in and out of the system were accounted for in order to calculate a material balance. The balance is shown in Table 6. Note that most of the values closed within 10 percent with the exception of calcium. The discrepancy in calcium may have resulted from accumulation in the scrubber column or other parts of the system and losses in the filter washwater.

Solids Removal

Some problems were found during the pilot plant operation which were directly related to the filtration step. The first problem was the filter cloth size. The initial filter cloth installed plugged with the solids causing equipment malfunction. This problem was overcome by using a coarser weave filter cloth.

A second problem encountered with the filtration step was the additional water introduced in the system most likely as a result of the continuous washing of the filter cloth. This problem would probably be minimized with larger-scale equipment.

An alternative to the horizontal belt filter for solids separation is the use of a centrifuge or centrifugal filter. A continuous decanter centrifuge may be acceptable for the operation. The separation of solids is controlled by the centrifugal force, the bowl radius, and the effective length. The specification depends on the desired product: maximum clarification, classification, or solids dryness.

The degree of dryness in this system is determined by the amount of water necessary in the cake to carry out sufficient Cl^- for an 8-1/2 to 9 percent chloride concentration in the filtrate.

A centrifugal filter was used in the pilot plant to remove excess liquor from the cake collected in the material balance run (Run 10) prior to analysis and disposal. The filter operated well, reducing the wet cake to about 30 percent moisture.

pH Control and Monitoring

The pH of the scrubbing solution was monitored during the pilot plant operation. An unsuccessful attempt was made to control pH by use of pH controllers. The pH varied greatly with small additions of NaOH until it reached a value of about 12. At this level, the system appeared to be buffered. Higher pH levels were not reached during operation. Because of the difficulty in controlling the pH, the effect of pH on scrubbing was not determined and the method of NaOH addition changed to pump feeding at a selected rate.

Continuous monitoring of the pH in the regeneration tank was also accompanied with difficulties. Apparently, the higher concentration of solids and extremely high pH's in localized areas (from the lime feed) adversely affected the electrodes and the meter. However, spot monitoring was accomplished with a portable unit.

The scrubber discharge pH (see Table 3) varied from less than 1 to over 4. This wide range probably results from the absence of a strong buffering effect at the column discharge. The discharge pH does not appear to correlate with either column plugging or removal efficiency.

Corrosion

Soon after the pilot plant started operation, the column solution turned purple, dark green, and black. The colors were a result of the corrosion occurring in the gas feed lines. It was originally believed that the dry acid gases could be retained in the stainless steel lines at least during the course of the study. However, moisture from the compressed air, uniting with the acid gases, caused corrosion at the point where the gases and air mixed. To alleviate this problem, the junction of the gas line and the air line was moved to just ahead of the column inlet. This is an indication of the need for corrosion-resistant pipes for a larger plant.

The column should also be made of corrosion-resistant material to avoid corrosion problems. The pH in the tower is expected to change from very basic at the top (pH 12) to acidic (down to about pH 1) before the liquor reaches the bottom of the scrubber.

CONCLUSIONS

Laboratory and pilot plant studies on the sodium dual alkali scrubbing process indicate that it is a feasible method of scrubbing the products of combustion of mustard agent. High removal efficiencies (over 99 percent) of both HCl and SO₂ may be obtained at stoichiometric ratios of alkali-to-acid gas of about 1.9 or higher. Removal efficiencies appear not to be affected by chloride in the scrubber liquor with loadings as high as 8.6 percent Cl⁻ (14.3 percent NaCl). Plugging of the scrubber occurs at chloride loadings of over about 9 percent Cl⁻ (15 percent NaCl); however, the solids redissolve as the chloride content falls. Cake moisture content at this chloride level was about 35 percent.

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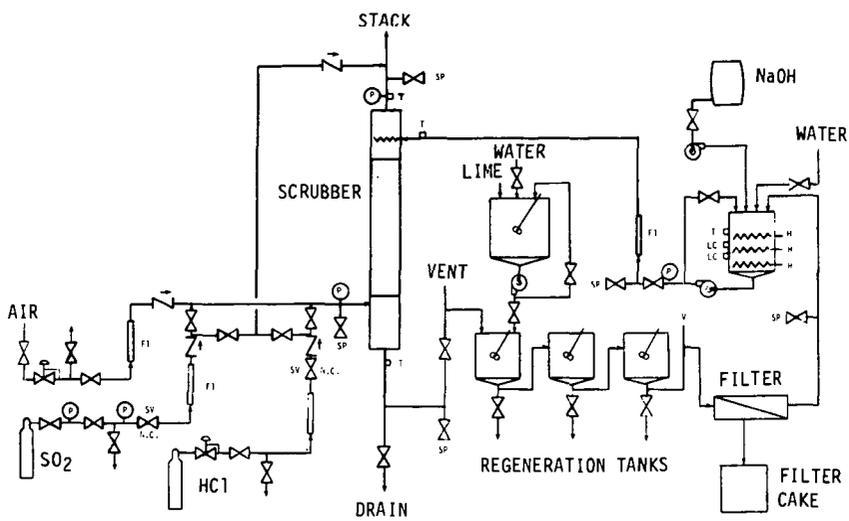


FIGURE 1. PILOT PLANT PROCESS FLOW DIAGRAM

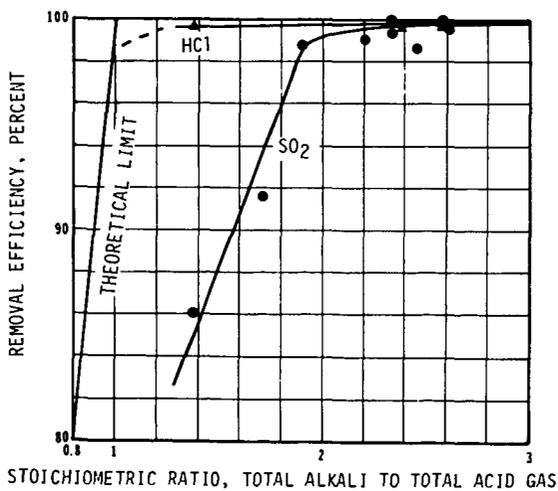


FIGURE 2. SO₂ AND HCl REMOVAL EFFICIENCY

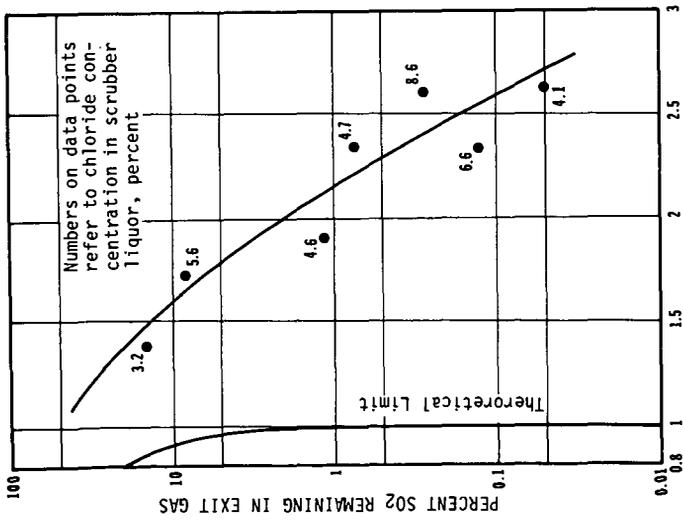


FIGURE 3. SO₂ REMOVAL

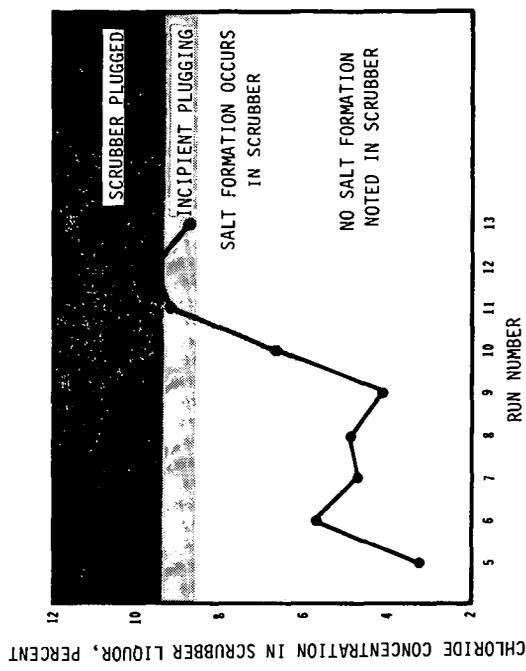


FIGURE 4. EFFECT OF CHLORIDE CONCENTRATION ON SCRUBBER OPERATION

TABLE 1A. RUN CONDITIONS

Run No.	Liquor Recirculation rate GPM	Gas Rate CFM	Column Temperature		pH		Ca(OH) ₂ feed #/hr.	NaOH feed #/hr.	Purpose of Run
			Inlet	Outlet	Inlet	Outlet			
1	1.0	31.4	158 F	108 F	10.4	-	5.46	*	To build concentration of liquor
2	1.7	31.0	158	108	9.5	-	10.98	*	To build concentration of liquor
3	1.4	30.6	160	99	12.0	10.4	6.18	3.9	To build concentration of liquor
4	0.9	30.6	160	96	10.9	5.2	9.44	4.2	To build concentration of liquor
5	1.3	30.6	158	106	10.9	2.3	6.18	0	Build concentration and removal efficiency data
6	0.9	31.1	163	94	11.0	1.3	6.18	4.25	Obtain removal efficiency data
7	1.2	31.1	162	95	10.4	1.2	7.72	3.65	Obtain removal efficiency data
8	0.9	31.1	159	95	12.0	4.2	9.44	4.65	Obtain removal efficiency data
9	0.6	31.1	161	96	12.1	4.1	10.98	4.75	Obtain removal efficiency data
10	0.4	31.1	159	96	12.1	1.9	9.44	4.65	Material Balance Run - removal efficiency data
11	1.1	32.4	161	-	12.1	0.2	9.44	11.5	Determine effect of high concentration of salts in liquor
12	0.6	32.4	163	-	12.2	0.6	9.44	11.5	Determine effect of high concentration of salts in liquor
13	0.7	32.4	160	-	12.1	3.5	9.44	5.4	Obtain removal efficiency data

* NaOH added to maintain pH

TABLE 1B. RUN GAS CONCENTRATIONS AND RESULTS

Run No.	SO ₂ Concentration PPM		HCl Concentration PPM		Stoichiometric Ratio		Removal Efficiency, %	
	In	Out	In	Out	total alkali/total acid gas	Ratio	SO ₂	HCl
1	5,290	-	25,700	-	-	-	-	-
2	4,450	-	15,600	-	-	-	-	-
3	4,500	50	15,800	-	2.20	2.20	98.89	-
4	4,500	68	15,800	-	2.46	2.46	98.49	-
5	4,500	632	15,800	24	1.38	1.38	85.96	99.85
6	8,290	700	15,600	-	1.72	1.72	91.56	-
7	8,290	95	15,600	-	1.89	1.89	98.95	-
8	8,290	60	15,600	-	2.34	2.34	99.28	-
9	8,290	4	15,600	26	2.61	2.61	99.95	99.83
10	8,290	10	15,600	138	2.34	2.34	99.88	99.12
11	8,290	-	54,300	-	1.03	1.03	-	-
12	8,290	-	54,300	-	1.03	1.03	-	-
13	12,960	34	37,800	-	2.61	2.61	99.73	-

TABLE 2. FILTRATE COMPOSITION
(Run 11)

SPECIES	PPM
Ca ⁺⁺	1,490
Na ⁺	41,200
Cl ⁻	83,200
SO ₃ ⁼	100
SO ₄ ⁼	1,300

TABLE 3. CHLORIDE CONCENTRATION OF SCRUBBER LIQUOR IN VARIOUS RUNS

Run Number	Cake Moisture Percent	Average Chloride Concentration in Scrubber Liquor, %	Scrubber Feed	Scrubber Discharge	Scrubber Liquor pH	Comments
5	50.7	3.2	10.5	2.0	No salt formation noted in scrubber.	
6	55.7	5.6	11.0	1.4	No salt formation noted in scrubber.	
7	47.9	4.6	10.4	1.2	No salt formation noted in scrubber.	
8	50.9	4.7	12.0	4.2	No salt formation noted in scrubber.	
9	48.3	4.1	12.1	1.6	No salt formation noted in scrubber.	
10	43.0	6.6	12.1	2.0	Some salt formation noted.	
11	35.3	9.2	12.2	0.2	Intermittent plugging in column.	
12	-	9.5	12.2	0.4	Scrubber full of salts.	
13	-	8.6	12.2	1.3	Salt formation reduction noted.	

TABLE 4. TYPICAL DRY CAKE SOLIDS COMPOSITIONS (RUN 11)

A. Analysis		PPM
Species		
Ca++		338,000
Na+		32,100
Cl ⁻		512
SO ₃ ⁼		336,000
SO ₄ ⁼		390,000

B. Postulated Dry Cake Composition		%
Species		
NaCl		1.6
Na ₂ SO ₄		7.9
Na ₂ SO ₃		14.8
CaSO ₃		42.3
Ca(OH) ₂		20.9
Unaccounted for		12.5
		100.0

TABLE 6. MATERIAL BALANCE (lb/hr)
Run 10

	S	Cl	Ca	Na
<u>IN</u>				
Gas	1.32	2.68	0	0
Alkali	0	0	5.10	2.67
TOTAL	1.32	2.68	5.10	2.67
<u>OUT</u>				
Gas	0	0.02	0	0
Cake Solids	0.96	0	2.67	1.38
Cake Liquor	0.04	2.92	0.01	1.37
Wash Solids	0.39	0	1.08	0.05
TOTAL	1.39	2.94	3.76	2.80

OVER (UNDER) lb/hr	0.07	0.26	(1.34)	0.13
OVER (UNDER) percent of material in	5.3	9.7	(26.3)	4.9

TABLE 5. SCRUBBER DEPOSIT

Analysis	Species	Percent
	Ca	24.3
	Na	3.17
	Cl	0.52
	SO ₃	23.4
	SO ₄	16.1
	Total S	21.1