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ORIGINAL CONTRIBUTION

AN ALTERNATIVE TO OPEN BURNING TREATMENT OF SOLID PROPELLANT MANUFACTURING WASTES

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ABSTRACT. Chemical Systems has selected base hydrolysis treatment to replace open burning of solid propellant manufacturing wastes. This treatment approach was adapted from several technologies. Reclaim/reuse and experimental treatment technologies were combined into the selected treatment process. Adoption of this change in treatment technology requires characterization and minimization of waste streams and alternate product development. The treatment facility design and permitting are discussed. Experiments performed on three representative types of solid propellants demonstrate the process feasibility and characterize the products of the hydrolysis. The products of the propellant treatment are ammonia, hydrogen, nitrogen oxide gasses, soluble inorganic and organic salts, and insoluble polymeric and metallic materials. Materials contaminated with propellant are cleaned and separated from the hydrolysate. The products of the process will be treatable in conventional waste treatment facilities. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Disposal of solid propellant wastes has been a simple task. Materials were placed in an open area and ignited from a remote site. The propellant materials burned well and left only a small percentage of remains. The task was so inexpensive neither the process nor the quantity of the waste was of much concern. Large quantities of material could be disposed of inexpensively. The major concerns were to control the safety hazard and the size of the conflagration. Large areas of many plants were dedicated to open burning. Pits and earthen barricades usually were formed to reduce the possibility of objects being thrown great distances by the occasional explosion. Detonation is the preferred disposal treatment for some materials, especially those that can transition to detonation at an unexpected point in the burn. Planned detonations are preferred over the unexpected.

Concerns about open burning of propellants increased with concerns about air quality. Issues were raised about the combustion products of the propellant and the associated materials burned with the propellants. The Environmental Protection Agency (EPA) and local agencies such as the Bay Area Air Quality Management District (BAAQMD) increased the attention given to open burning of all kinds. The open burn facility (OBF) at Chemical Systems, San Jose, California, has operated for many years under EPA interim status as a treatment facility. The BAAQMD also recognized this facility. Both agencies applied various regulations to the operation of the OBF. About 1989, these agencies began to look differently at Chemical System's OBF. The BAAQMD through public hearings wrote specific language into the district's Regulation 5: OPEN BURNING. The regulation as it went into effect on December 19 1990, is quoted below.

BAAQMD REGULATION 5
OPEN BURNING

405. Propellants, Explosives and Pyrotechnics Compliance Schedule: Any person seeking to dispose of material within the provision of 5-401.14 (hazardous materials) shall comply with the following:

405.1. By April 1, 1994, and thereafter annually submit a report to the APCO (Air Pollution Control Officer) that shall contain the following information:

ACCEPTED 19 JUNE 1997.

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405.1.a. Review of alternative technology for the disposal of propellants, explosives and pyrotechnics, other than open burning which minimize the impact on air quality.

405.1.b. Schedule for the development and implementation of alternative disposal method to comply with 5-401.

405.1.c. Waste minimization efforts.

405.2. Records must be maintained as per section 5-501.

405.3. Verbal notification shall be given prior to each burn.

405.4. Upon written determination by the APCO that any treatment or disposal method other than open burning is feasible, installation or implementation shall be completed within two years, but in no case later than January 1, 1995.

The regulation was amended in 1994. The amendment extended the date required for implementation of an alternative to open burning to January 1 1997. The amendment required that applications for a permits to construct and operate be made to the BAAQMD by January 1 1996, and required the installation of an on-site waste treatment system be completed and in operation no later than January 1 1997. This regulation, particularly Section 405.4, and the public opinion that went into its drafting enhanced the attention Chemical Systems paid to propellant manufacturing wastes and their disposal.

Chemical Systems vigorously addressed the areas of Waste Minimization, Alternate Use, and Alternate Treatment. These issues will be discussed. Alternate Treatment is the main subject presented here. The technologies investigated, selection of a treatment process, characterization of the products of this process, and permitting of the treatment process are outlined.

WASTE MINIMIZATION

Before a treatment process could be selected the quantity and character of what required treatment had to be defined. The records of the OBF gave a quantitative value for the history of open burning treatment at Chemical Systems. The quantities of waste being treated showed that the cost of a treatment other than open burning would be very high. Therefore, the quantities of waste being treated had to be minimized. Starting in 1989 efforts took place to reduce the quantity of waste requiring treatment. Figure 1 shows the progress made in reducing the waste.

The waste minimization efforts touched all aspects of the process from design and development to cleanup after stripping the tooling from a motor. Batch size requirements were reduced to minimize excess. Casting lines were shortened. Materials not contaminated with propellant were eliminated from the waste sent to the OBF.

The record keeping of the OBF was enhanced in 1991 to include more information. This enhancement allowed the OBF treatment to be analyzed. The materials other than propellant being sent to the OBF were characterized and their sources were studied to eliminate extraneous materials. This data and other observation quickly showed the large quantities and diverse character of the waste. Figure 2 shows the types of materials and quantities being sent to the OBF. Efforts began to reduce the quantities of non-propellant materials being sent to the OBF. The greatest effect on reducing these materials came through getting the operators involved in the minimization efforts. Suggestion awards were made and awareness of what was needed to reduce this material was heightened. Procedures and methods were changed to reduce the waste. Segregation of non-contaminated trash from the propellant contaminated waste had the greatest impact on the materials going to the OBF.

The OBF activities also changed physically during 1991. The number of treatment sites was reduced from twelve to two. The quantity to be burned at any one tine was limited to 3000 pounds of United Nations hazard Class 1.1 explosive waste or 6000 pounds of United Nations hazard Class 1.3 explosive waste in any one pit. A restriction that burns could only be performed on "burn days" as defined by the BAAQMD already existed. Therefore Chemical System's ability to dispose of explosive waste was severely limited. The historical number of burn days is a maximum of about 10 per year. The wind direction requirements, and the maximum of 12,000 pounds in any one burn fixes the physical limit at about 120,000 pounds per year. Therefore, Chemical Systems had the need to find alternate uses for much of the material that it had previously treated in the open burn facility.

ALTERNATE USES

Chemical Systems has six basic materials in excess from the propellant manufacturing process. They are Class 1.3 propellant, Class 1.1 propellant, Water wet machine turnings of 1.3/1.1 propellants, 1.3/1.1 propellant contaminated materials, and a category of research, experimental, or sensitive materials. Chemical Systems set about finding a use for these materials. Success was achieved for five out of the six. The use was found in the commercial blasting industry. The conversion of these materials to blasting

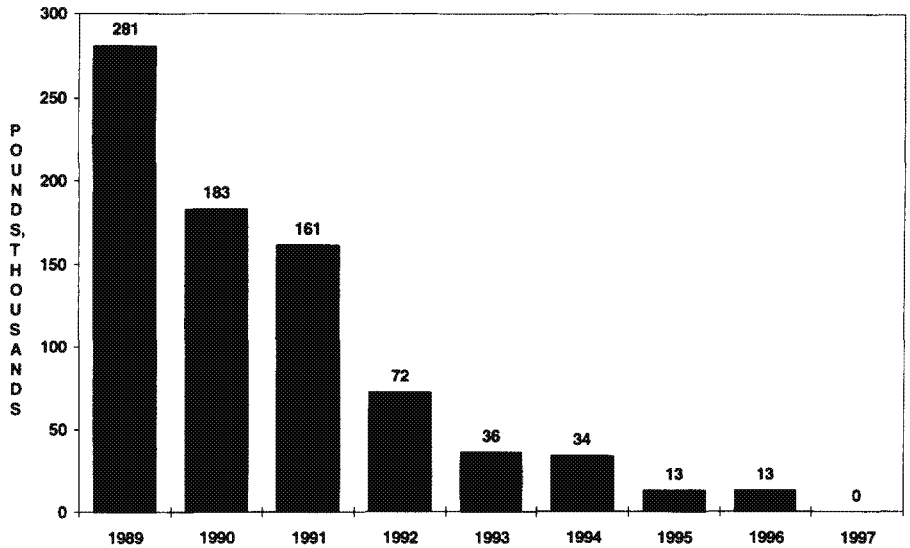

FIGURE 1. Propellant waste open burned 1989 to 1997.

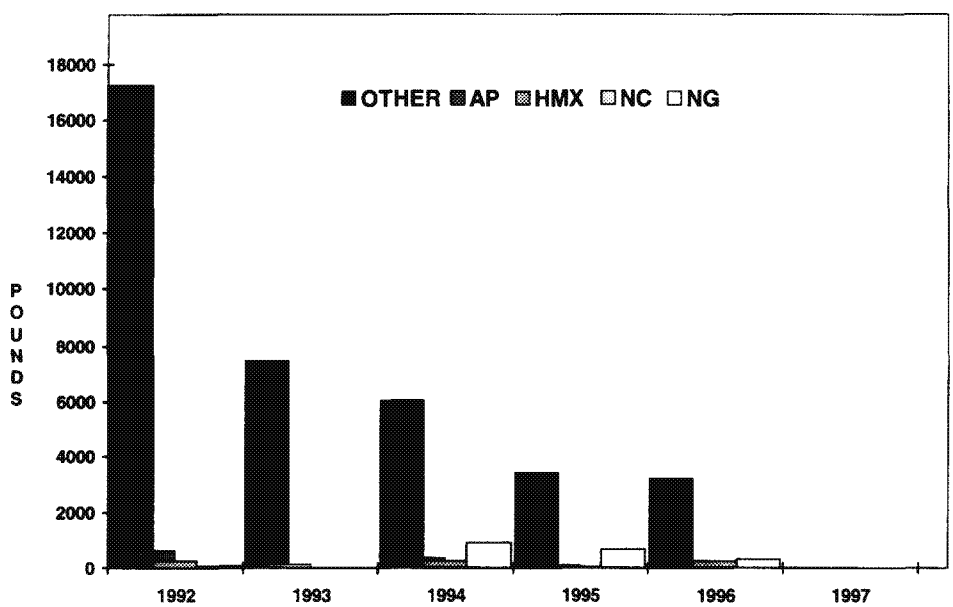

FIGURE 2. Open burn materials.

materials is outlined in Fig. 3. Alternative use grew in proportion to the amount requiring open burning. Even as production quantities went down the portion being sent to alternative use increased to 95 to 97 % of material excesses from the manufacture of rocket motors. This is shown in Fig. 4.

ALTERNATE TREATMENT

The quantity of materials requiring waste treatment was reduced to 3–5% of the material not going into rocket motors by the alternate use of propellant materials in the blasting industry. The materials that remain are of varying composition and not economical nor practical to classify for shipment off site for treatment. Therefore the treatment process that Chemical Systems was seeking needed the capacity of less than 40,000 pounds per year. The process had to be capable of handling the significant portion that was the contaminated materials, such as wood, rubber, rags, plastic, paper and other materials (metals). The process would treat mainly Class 1.1 and sensitive materials that must be desensitized and rendered non-ignitable. A process that produced a non-hazardous product was desired.

The BAAQMD and EPA require Chemical Systems to monitor, evaluate and report on alternative technologies that might be used to replace open burning. Many technologies are being worked by several agencies, services and private sector contractors.

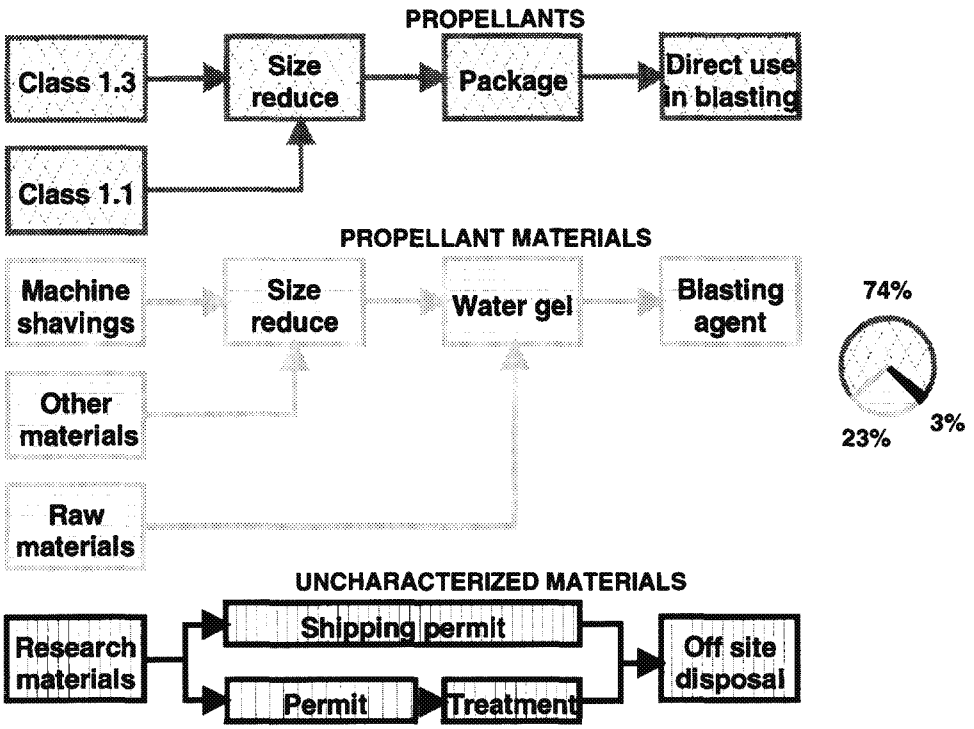

FIGURE 3. Alternate use paths.

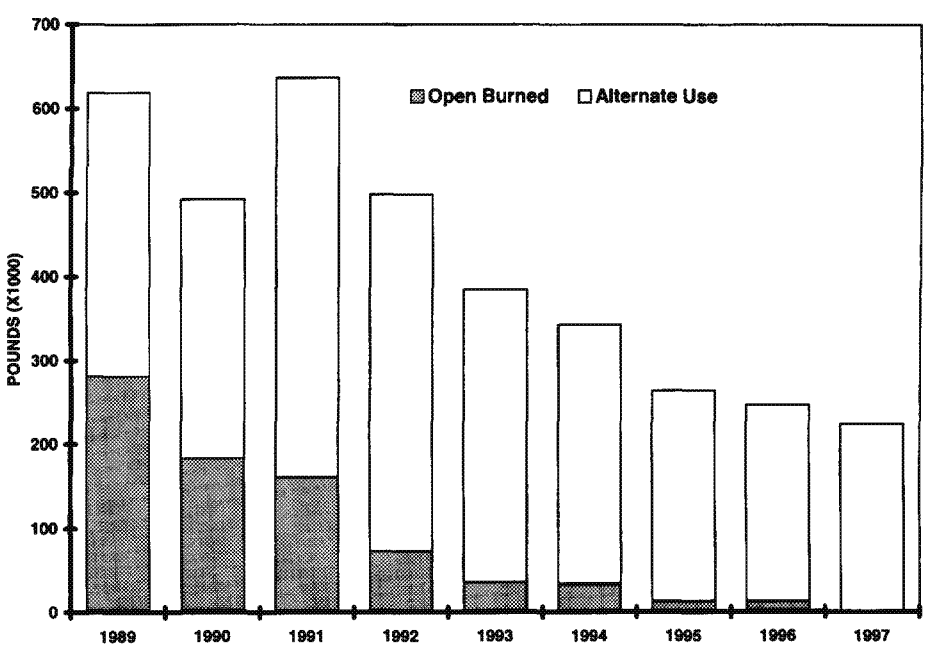

FIGURE 4. Alternate use quantities.

All of these technologies have their particular niche or applicability. Chemical Systems has grouped these technologies into four categories for the reporting. The categories are Recycling, Biodegradation, Enclosed oxidation, and Open burning.

Because no one technology was found to be as economical or as efficient as open burning Chemical Systems selected segments of a combination of technologies to address the issue. Water jet cutting, ammonium perchlorate extraction, and base hydrolysis were the selected technologies. This combination provides the ability to process the relatively small quantities efficiently. The water provides a safe way of separating the non-hazardous materials from the materials requiring treatment. The base, sodium hydroxide, provides the desensitization of both the Class 1.1 and Class 1.3 materials. The resulting products are non-hazardous except for the high pH

which classifies the products as corrosive and therefore hazardous waste. Neutralization could be considered if it becomes an economic advantage in disposal costs. A design has been completed for the facility, including equipment requirements and process controls. The facility required is small and therefore an existing site and structure was utilized.

The process is simple. Propellant waste materials are transported to the facility as required for disposal. These materials are packaged in conductive plastic bags of less than 20 pounds each. The process capacity is designed for 200 pounds per 8 h shift. The bags of material are placed in the tumbler reactor. The tumbler is rotated as water jets inside are directed at the materials. The flights in the inner tumbler mesh cylinder continue to return materials too large to pass through the mesh, back under the water jets to be macerated. Materials in the bottom of the tumbler are immersed in the base solution which begins the hydrolysis reaction as the material is cut into smaller pieces. The small material which passes through the mesh is carried to the far end of the tumbler and metered out by the rotating baffle. The gas produced by the hydrolysis process is drawn out of the tumbler reactor up a stack diluted and vented to the atmosphere. The solution is pumped to a digestion tank to complete the hydrolysis. Any additional gas is also vented. When all the material in the mesh cylinder is cleaned by the water jets and desensitized by the base solution, the tumbler reactor is reversed and these materials are transported to the far end of the vessel and fed into a container for inspection and disposal as non-hazardous waste. The solution in the digestion tank on completion of the reaction is pumped to the holding tank. There it is analyzed for content. The solution will, when the analysis is completed, be pumped into a tanker for disposal at a hazardous waste treatment facility. Conversely, the solution could be neutralized on site and possibly discharged as a non-hazardous waste. A schematic of this facility and the equipment is shown in Fig. 5.

The hydrolysis process has been characterized for three propellants that are typical of those found in the propellant hazardous waste at Chemical Systems. These are a polybutadiene acrylic acid acrylonitrile binder Class 1.3 propellant (UTP-3001), a hydroxyl terminated polybutadiene binder Class 1.3 propellant (UTP-25201), and a polyether binder nitroglycerin-nitramine containing Class 1.1 propellant (UTP-25540). The characterization of these propellants was performed by reacting 100 grams of propellant with the required quantity of 2 molar sodium hydroxide solution. The gasses evolved and the resultant solutions were analyzed.

The expected reaction products are shown in Table 1. The products of the Class 1.3 propellants are very straight forward. Aluminium hydrolyzes to produce aluminium hydroxide and hydrogen gas. Ammonium perchlorate produces sodium perchlorate and ammonia or ammonium hydroxide in solution. The two binder's polybutadiene acrylic acid acrylonitrile (PBAN) and hydroxyl terminated polybutadiene (HTPB) disassociate to varying degrees producing some soluble organic materials and mostly a rubber like crumb. The products of Class 1.1 propellants containing materials such as nitroglycerin and the nitramine hydrolyze to produce gasses;

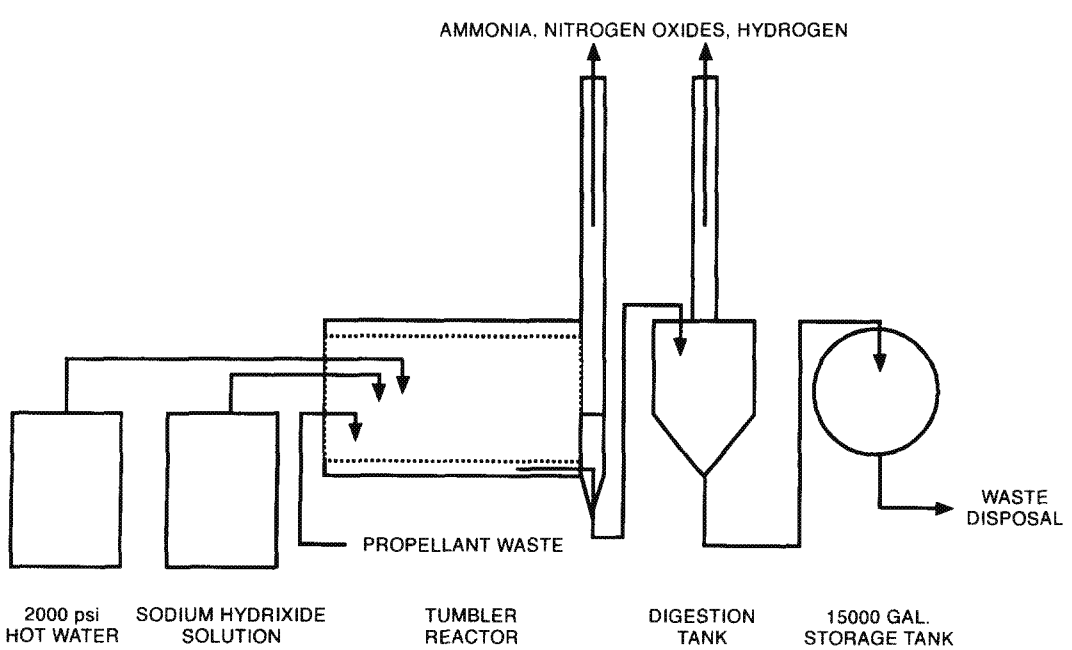

FIGURE 5. Hydrolysis treatment facility schematic.

TABLE 1
Base Hydrolysis of Propellants

ALUMINIUM

$$Al + NaOH + H_2O \rightarrow Al(OH)_3 + H_2 \uparrow + NaOH$$

Products: aluminium hydroxide and hydrogen

AMMONIUM PERCHLORATE

$$NH_4ClO_4 + NaOH + H_2O \rightarrow NaClO_4 + NH_3 \uparrow + NaOH + H_2O$$

Products: sodium perchlorate and ammonia

BINDER

$$-OCH_2(C_2H_4)_nOCONH(CH_2)NHCO- + NaOH + H_2O \rightarrow HOCH_2(C_2H_4)nOCONH(CH_2)NHCO- \downarrow + NaOH + H_2O$$

Products: binder crumb

NITROGLYCERIN

$$C_3H_5O_9N_3 + NaOH + H_2 \rightarrow C_3H_8O_3 + NO_2 \uparrow + H_2O$$

Products: glycerin and nitrogen dioxide

HMX

$$C_4H_8O_8N_8 + NaOH + H_2O \rightarrow NaCHO_2 + CH_3OH + N_2O \uparrow + NH_3 \uparrow + H_2 \uparrow + NaNO_3 + NaNO_2 + H_2O$$

Products: sodium formate, methanol, nitrous oxide, ammonia, hydrogen, and sodium nitrate and nitrite

ammonia and nitrogen oxides, soluble organic compounds; glycerin and methanol, and salts; sodium nitrate, nitrite and formate. The results of the analysis of the solutions was not as straight forward as the chemistry would appear. Table 2 shows the results of the hydrolysate analysis.

The analysis of the gas evolved from the Class 1.1 propellant hydrolysis, showed the production of the nitrogen oxides as predicted. The NO_x produced was 0.8 g per 10 g of propellant. Gas analysis also showed that the Volatile Organic emissions were below required minimums. Although analysis of the laboratory scale testing did not provide the expected quantitative results sufficient information was available on the gaseous products to calculate engineering derived emission factors.

DERIVATION OF EMISSION FACTORS

The Emission Factors which will be used to calculate the emissions for the Hydrolysis Treatment Facility (HTF) are based on information from three sources. The sources are the quantities of materials treated at the Open Burn Facility (OBF) in 1993 and 1994, the chemistry of the major ingredients of propellants and analysis of propellant hydrolysis laboratory tests. The data in Table 3 is from the OBF records. The size of the facility required and the maximum quantity to be treated were set from this data. The data was used in estimating the composition of the materials to be treated. The proportions of Class 1.1 propellant, 1.3 propellant and other materials are factors in this estimate.

TABLE 2
Hydrolysate Analysis

Propellant	UTP-3001	UTP-25201	UTP-25540
Analysis	$mg\,l^{-1}$	$mg\,l^{-1}$	$mg\,l^{-1}$
NO_3	0	0	1,500
NO_2^-	0	2	6,000
Other anions	18	20	14,160
Organic carbon	510	130	10,000
Total dissolved solids	36,000	35,000	42,000
Total solids	38,000	36,000	49,000

TABLE 3
OBF Treated Materials

	1993	1994	Average
Propellant 1.1 (pounds)	16,100	5,004	10,552
Propellant 1.3 (pounds)	12,800	23,211	18,006
Propellant total (pounds)	28,900	28,215	28,558
Other materials (pounds)	7,600	6,019	6,810

Engineering Estimates

The ammonium perchlorate (AP) and aluminium (Al), the major ingredients in propellants, react with sodium hydroxide and water in a straight forward manner to produce ammonia (NH_3) and hydrogen (H_2) gas, respectively. NH_3 is produced in a mole for mole ratio from the AP. Therefore 17 units of NH_3 is produced for each 117.5 units of AP. H_2 is produced on a 1.5 mole per mole of Al basis. Therefore 1.5×2 units of H_2 is produced for each 27 units of Al. Considering the proportions of each of these ingredients in propellants and the OBF data an Emission Factors are calculated. These calculations are shown in Table 4.

Analysis

Nitrogen oxides are produced from the propellants that contain nitrogen oxides in the ingredients such as nitroglycerin and nitramines. These ingredients are found in the 1.1 propellants. Therefore the emission factor for nitrogen oxides was derived based on the proportions of 1.1 propellant to be treated, OBF data, the composition of these propellants and the chemistry of the reactions with sodium hydroxide. The chemistry of 1.1 propellant ingredients is more complex than that of the inorganic ingredients of 1.3 propellants, AP and Al, therefore analysis of the gas evolved during the reaction was performed to determine an emission factor for the nitrogen oxides. Ten gram samples of 1.1 propellant were reacted with 200 ml of 2 molar sodium hydroxide solution. The nitrogen oxides (NO_x) evolved were measured in the air purged from the reaction vessel. The quantity of NO_x measured was 0.8 g for the 10 g of propellant, or 0.08 g^{-1}. The **Emission Factor** for $\mathbf{NO_x}$ is calculated as **0.08**. Therefore for each pound of material processed through the HTF 0.10 pounds of ammonia, 0.02 pounds of hydrogen, and 0.08 pounds of nitrogen oxides will be considered to have been emitted. The contents of the solution will be determined by analysis.

TABLE 4
Calculated Emission Factors

	Mole ratio	Average wt% reactant	Emission factor
NH_3	$17/117.5 = 0.14$	AP = 69	$0.14 \times 0.69 =$ **0.10**
H_2	$1.5 \times 2/27 = 0.11$	Al = 18	$0.11 \times 0.18 =$ **0.02**

CONCLUSION

The alternative to open burning of propellant manufacturing wastes is available to Chemical Systems. The alternative uses of propellant products in commercial blasting agents has minimized the materials requiring treatment. Base hydrolysis treatment of the minimum quantity of uncharacterized wastes has been approved by the permitting agencies. The design of the facility is completed. The appropriate permits for a waste treatment system on-site have been approved. A permit to construct has been approved by the BAAQMD. The permit to operate will be requested at completion of checkout. A modification of the Part B permit under interim status was made by the Department of Toxic Substance Control, California EPA. Construction of the facility is in progress with checkout and start up scheduled before the end of 1996. The required target date of January 1 1997, for Chemical Systems to have eliminated open burning, install an on-site waste treatment system, and have it operational will be met.