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**A STATE-OF-THE-ART REVIEW
OF MATERIALS-RELATED PROBLEMS IN
FLUE GAS DESULFURIZATION SYSTEMS**

by

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Materials Science Division

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ABSTRACT

This report characterizes the chemical and mechanical environments to which the structural components used in flue-gas desulfurization (FGD) are exposed. It summarizes the necessary background information pertinent to various FGD processes currently in use, with particular emphasis on lime/limestone scrubbing technology, so that the materials problems and processing variables encountered in FGD systems can be better defined and appreciated. The report also describes the materials currently used and their performance to date in existing wet scrubbers. There is little doubt that with more extensive use of coal and flue-gas scrubbers by utilities and other segments of private industry, a better understanding of the material failure mechanisms, performance limitations, and potential problem areas is required for the design of more reliable and cost-effective FGD systems.

To meet the above objectives, a materials evaluation program is proposed. The important experimental variables and the number of tests required to evaluate a given material are discussed.

I. INTRODUCTION

Although sulfur forms several oxides with oxygen, the most stable oxides formed by burning coal are SO_2 and SO_3 . Because of thermodynamic considerations and the extremely slow rate of conversion of SO_2 to SO_3 , SO_2 is the principal sulfur-oxygen compound in flue gases from coal-fired boilers. Thus, flue-gas desulfurization (FGD) can be defined, for practical purposes, as the removal of SO_2 from these gases before they enter the atmosphere.

The treatment of flue gases to reduce SO_2 emissions has a history of nearly half a century: The basic principles and process parameters governing FGD were developed at the London Power Company and Imperial Chemical Industries in England during the 1930s. However, interest in this work was stimulated in the U.S. during the years 1960-1975 as a result of two events. First, the energy shortage accelerated the utilization of high-sulfur coal (Table I), which is abundantly available in this country. Second, strict federal and state air-quality standards were imposed on coal-fired power

Table I. Composition of a Typical Western Kentucky Coal
(Ref. 27)

Constituent	Percent by Weight
H	4.5
N	1.3
C	66.0 ^a
O	7.5
S	3.3
Ash	12.0
Moisture	5.4
	<hr/> 100.0

plants as a necessary step toward SO₂ pollution abatement. Faced with the necessity of installing FGD systems in most of their coal-fired power plants in the early 1970s, the utility companies confronted many problems, some of which were related to the selection of materials suitable for the highly corrosive and abrasive environment of the scrubber assembly. However, with experience gained from the operation of large-scale pilot plants, the problems were better defined and research efforts were initiated toward solving them. These efforts led to the development of new materials and several protection schemes to enable these materials to withstand a hostile environment that contains sulfurous and sulfuric acids, chlorides, and particulates. Extensive studies of alkali scrubbing for SO₂ removal have been conducted¹⁻⁸ through U.S. government-sponsored research and development programs and by several private concerns. As a result of these investigations, lime/limestone scrubbing technology has advanced faster and has been more fully characterized than any other SO₂-removal method.

The literature dealing with FGD systems and related problems is very extensive and a comprehensive survey of this vast field is outside the scope of this report. Instead, the report will review the status of knowledge concerning materials selection and performance. In particular, our objectives are to characterize the chemical and mechanical environment to which FGD components are exposed, and to define the potential problems and the extent to which they have been overcome or mitigated.

II. FGD PROCESSES

A. Classification

Virtually all coal-burning power boilers, except those operating on very low-sulfur western coal, produce SO_2 levels above the acceptable limits set by most states (see Table II). Therefore, most power plants are required to use one of the several technologically feasible SO_2 -removal processes, which are briefly described in Table III.⁹⁻¹⁵ Essentially, most of the methods^{9-12,16-20} involve scrubbing a high- SO_2 gas with some type of alkali material such as lime or soda ash. FGD methods can be classified as either throwaway or recovery processes, based upon the end product derived after the removal of SO_2 . The throwaway processes produce a by-product sludge, which must be either deposited in a nearby pond or landfill or trucked to remote disposal sites. Recovery processes yield a usable product, which is most often sulfur but can also be sulfuric acid, a fertilizer base compound, or gypsum. FGD methods can also be classified as dry or wet, with reference to the medium used for SO_2 absorption; the most widely used and demonstrated processes are of the wet type.

Table II. Composition of Stack Gas Evolved in Burning
Western Kentucky Coal (Ref. 27)

Constituent	Formula	Percent by Volume
Nitrogen	N_2	74.6
Carbon dioxide	CO_2	12.6
Oxygen	O_2	4.9
Water vapor	H_2O	7.8
Sulfur oxides		
Sulfur dioxide	SO_2	0.22
Sulfur trioxide	SO_3	0.001
Nitrogen oxides	NO_x ($x = 1,3$)	0.04
Particulate matter		36 g/SCF

Table III. Leading SO₂-removal Processes

Process	Operating Principles	SO ₂ /Particulate Removal Efficiency	Comments
Lime/Limestone	Wet absorption in a slurry of CaO/CaCO ₃ ; end products are insoluble sulfites and sulfates, which are disposed of as a waste.	Up to 90% SO ₂ removal and 99% fly-ash removal in most scrubbers.	Probably the cheapest of existing processes, but is associated with waste, scaling, and water pollution problems.
Double Alkali Process	Wet absorption in scrubber containing NaOH; reactants are soluble; reaction products precipitated and removed from recycled reactant solution outside of scrubber; end product is gypsum.	High-efficiency (>90%) SO ₂ removal and high particulate removal as above.	Scaling is a problem in the precipitator, but not in the scrubber.
Magnesia Scrubbing	Wet absorption by MgO slurry; fly ash removed prior to or after scrubbing; MgO regenerated by calcining with carbon. SO ₂ by-product can be converted to sulfuric acid or sulfur.	90% SO ₂ removal; particulate removal as required by pre-scrubber.	May be more reliable than lime/limestone process; no known waste disposal problems; higher cost for regeneration; marketing of sulfur products required.
Catalytic Oxidation	SO ₂ is converted to SO ₃ in the presence of V ₂ O ₅ catalyst and SO ₃ is converted to sulfuric acid.	80-90% SO ₂ removal; particulates removed prior to conversion from SO ₂ to SO ₃ .	Catalytic oxidation occurs at 850°F.
Wellman-Lord/SO ₂ Reduction	SO ₂ is absorbed by Na ₂ SO ₃ , recovered by heating, and reduced to S.	>90% SO ₂ removal; particulate removal by pre-scrubber.	Wellman-Lord process produces concentrated SO ₂ by thermal stripping of NaHSO ₃ . SO ₂ is reduced to S with natural gas.
Citrate	SO ₂ is absorbed by sodium citrate and citric acid and reacted with H ₂ S to produce elemental sulfur.	90% SO ₂ removal; particulate removal by pre-scrubber.	
Dry Absorption	The absorption medium is char; the absorbed SO ₂ is recovered and reduced to elemental sulfur.	Lower efficiency of SO ₂ removal than the above processes.	Minimum water use, minimum waste disposal, no stack reheating.
Dry Scrubbing	Na ₂ CO ₃ solution sprayed into the flue gas in a drying chamber to produce Na ₂ SO ₃ /Na ₂ SO ₄ powder.	75-85% SO ₂ removal.	No reheating and no sludge-handling problem. Applicable to low-sulfur coals.

B. Description of the Lime/Limestone System

As pointed out earlier, lime/limestone scrubbing is the most highly developed and widely applied FGD method in current use. In fact, this method is used in ~90-95% of present installations (including those under construction). From a materials viewpoint, the lime/limestone scrubbers are the most useful systems to investigate because of the extensive operating experience available.^{16,21,22} Many of the lime/limestone FGD system components (e.g., prescrubbers, absorbers, spray nozzles, mist eliminators, reheaters, fans, ducts, expansion joints, dampers, pumps, piping, valves, tanks, thickeners, agitators, rakes, and filters) are also used in some of the more advanced processes.

The three main components of the lime/limestone scrubbing system are the scrubber, the reaction tank, and the thickener. The function of the scrubber is to promote intimate mixing of the SO₂-laden flue gas and the lime/limestone, which is introduced into the scrubber as a slurry of 5-15 wt.% solids in water. The exhaust gas from the boilers passes through the scrubber, undergoes cleaning, and then proceeds to the stack (see Fig. 1). The reaction tank forms the receptacle for the reacted materials discharged from the scrubber. The chemical reactions between the SO₂ and the lime/limestone slurry go to completion here. Reusable slurry is sent back to the scrubber, and makeup slurry is added to the tank as needed. The reacted slurry is then transported to the thickener, where the solids are concentrated by sedimentation and removed to a pond or landfill. The clarified water is returned to the scrubber for reuse.

Fig. 1. A Schematic Illustration of the Flue-gas Path in a Typical Coal-fired Power Plant. From Power Engineering, September 1976, Volume 80, Number 9, pages 52-55.

C. Design Considerations for Lime/Limestone Systems

The chief criterion for choosing among the several available types of lime/limestone scrubbers (venturi, spray tower, open grid, etc.) is the high efficiency of SO₂ removal. High efficiency has been obtained with two-stage and multistage venturi scrubbers. However, the design of a specific system depends on many variables such as the sulfur and ash content of the coal, required turndown capability, type of waste disposal available, fly-ash content (fly ash can be removed either before SO₂ or at the same time), liquid-to-gas (L/G) ratio, pH control, % solids in slurry, lime/limestone particle size, number of stages, and gas-liquid interface.^{23,24} For example, the propensity for scaling increases with a decrease in the L/G ratio. However, the rate of absorption can be boosted by increasing the gas-liquid interface. Many of the parameters mentioned above are interrelated and require a study to optimize the efficiency of operation.

Another operating consideration which affects the choice of materials for lime/limestone systems is whether the stack gas is reheated.^{25,26} As the flue gas passes through the absorber and demister, it is humidified and cooled to 120-130°F, thus losing its buoyancy. For example, under standard atmosphere conditions, flue gas at 310°F (154°C) has a velocity of 42 fps (13 m/s) ... a stack, which is typically 16.5 ft (5 m) in. diameter and 300 ft (91 m) high, whereas the same gas at 125°F (51°C) has a velocity of only 32 fps (9.8 m/s). Therefore, the wet-scrubbed gas must be reheated to regain its buoyancy in the stack; this decreases the visible plume and amounts of mist and condensate (acid rain) in the stack. The reheating procedure also reduces corrosion of ducts, fans, and stacks downstream by keeping the temperature of the gas above its dew point.

FGD systems are also provided with several expansion joints (see Fig. 1). In addition to relieving thermal stresses, they perform a number of functions such as isolation of mechanical vibrations, reduction in mechanical noise, and compensation for misalignment. Since these joints are subjected to varying corrosive and erosive conditions at temperatures ranging from 50 to 450°C, evaluation of materials for them is very important.

III. CHARACTERIZATION OF FGD ENVIRONMENTS

The most important parameters governing the corrosion of materials in scrubber environments are the pH and chloride content of the liquid and slurry. However, the corrosion process is further accentuated by oxygen and crevice concentration effects as well as by erosive conditions prevalent in the environment, mechanical loading, and temperature excursions. In this section, the chemical, mechanical, and thermal environments of lime/limestone and other scrubbing systems will be examined to provide a basis for defining the potential materials problems.

A. pH

The pH of the solutions used in the scrubbing assembly is predominantly determined by the chemistry of the FGD process, the impurity content in the coal and water, and the chemicals used in the system. In practice, under normal operating conditions, the pH can vary from ~3 (highly acidic) to 9 (basic), depending on the system and the location within it. These differences in pH should affect the operation of the scrubber with regard to both scale formation and corrosion problems. Thus, a variety of materials capable of withstanding solutions that vary from acidic to alkaline are needed. The requirements for pH control associated with several different scrubbing processes are described in the following subsections.

1. *Lime/Limestone Process*

A knowledge of the detailed mechanism for wet scrubbing with lime (CaO) and limestone (CaCO₃) is important for understanding the operation of the system and the associated materials problems. Fellman and Cheremisinoff^{27,28} have postulated the following reaction sequence for scrubbing with CaO:

Summation of reactions (1-6) leads to the overall reaction

$$(\Delta G_{300 \text{ K}} = -44.5 \text{ kcal/mole}) ,$$

where ΔG is the free energy change of the reaction at room temperature.

The postulated chemical reactions for scrubbing with CaCO_3 are²⁸

Summation of reactions (8-13) leads to the overall reaction

$$(\Delta G_{300 \text{ K}} = -13.4 \text{ kcal/mole})$$

Although both overall reactions are thermodynamically favorable, reaction (7) is much more favorable than reaction (14). However, limestone is less expensive and more readily available than lime, and the low efficiency of reaction (14) can be improved by proper scrubber design.

The effect of pH on these two processes is complex. For example, simultaneously with the above reactions, sulfite ion undergoes oxidation by dissolved oxygen in the absorbent slurry to form sulfate ion:

Because of the excess oxygen in the flue gas, the concentration of dissolved oxygen in the slurry is approximately constant, so that the formation of SO_4^{2-} by reaction (15) depends on the availability of SO_3^{2-} . In practice, calcium sulfite and sulfate coprecipitate in the system. From the relationship between solubility and pH for calcium sulfite and sulfate (Fig. 2), it is clear that sulfite is more soluble in water than sulfate at low pH, and acid conditions therefore enhance sulfate production. This is undesirable because CaSO_4 forms a hard scale. (This problem can be mitigated somewhat by increasing the L/G ratio.) However, if the pH is too high, the increased

Fig. 2. Effect of pH on Solubility of $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 122°F (Ref. 28).

precipitation of CaSO_3 causes a phenomenon known as soft pluggage. Also, in both the lime and limestone reaction sequences, there is a critical step [reactions (5) and (11), respectively] in which Ca^{2+} captures SO_2 from the solution. In the limestone system, formation of Ca^{2+} depends on H^+ and CaCO_3 , whereas in the lime system, formation of Ca^{2+} depends only on the presence of lime. These results imply that the optimal pH (5-6) for operation of a limestone system is lower than that for a lime system.

2. Double Alkali Process

The scaling in lime/limestone scrubbers caused by the presence of insoluble calcium sulfite/sulfate is eliminated in the scrubbing part of the double-alkali process (Table III). Sodium hydroxide is used for scrubbing and the resultant liquor is reacted with calcium-based alkali to precipitate CaSO_4 for disposal and to regenerate the sodium-based alkali. The chemical reactions associated with the scrubbing and regeneration processes are as follows:

One of the primary reasons for the development of the alkali process was to obviate the scaling problem. However, scaling can occur in the regenerator, and the problems encountered there are similar to those in the lime/limestone system.

3. Magnesia Process

Magnesia scrubbing (see Table I) utilizes a magnesia slurry to form magnesium sulfite (and sulfate). The slurry solutions are evaporated to obtain MgSO_3 and MgSO_4 crystals. These crystals, upon calcination at 1475-1832°F in the presence of coke, regenerate MgO and release SO_2 , which is converted to sulfuric acid. In the MgO system, fly ash and other particulates are removed from the flue-gas stream prior to the scrubbing operations by either electrostatic precipitators or primary scrubbers. In the magnesia scrubbing system, the pH periodically undergoes excursions from 0.5 to 9 and the corrosion problems appear to be similar to those of systems described earlier in the report.

4. Citrate Process

The citrate process is a regenerable process (Table I) that yields high-quality sulfur as a by-product. Sulfur dioxide from the flue gas is absorbed by sodium citrate + citric acid. Citrate acts as a buffering agent, which facilitates control of the process pH -- a desirable feature from the viewpoint of materials performance -- and shifts the equilibrium to the right as shown below:¹⁸

The SO_2 laden liquor from the absorber is brought into contact with H_2S in a reactor at atmospheric pressure and 150°F, and all the SO_2 is converted to sulfur and water:

It is claimed that this process consumes less chemicals and less power than lime/limestone scrubbing (power consumption increases with an increase in L/G; L/G = 7 for citrate and 100 for limestone scrubbing). Also, the citrate process creates no sludge-handling problem. Insufficient operating experience exists to evaluate the economics and reliability of the process, although there is sufficient incentive for a long-term study of this process.

B. Chlorides

The FGD environment is not only acidic, but is rich in highly soluble chlorides derived from several sources. Chlorine is a minor constituent of coal. During coal combustion, chlorine enters the gas phase predominantly as HCl, which can attain a concentration of as much as 100 ppm in the flue gas; the chlorine also forms inorganic chlorides in the particulate matter entrained in the flue gas. Most of the HCl and chlorides in the gas enter the FGD system. Chlorides are also produced by the scrubbing materials. For example, if MgO scrubbing is used, magnesium chloride is formed. In addition, chlorides in the form of HCl and NaCl can enter the scrubbing system as impurities in the makeup water. In order to minimize water pollution, closed-loop recirculating systems are widely used. In such operations, the amount of makeup water added is roughly equal to the amount of water evaporated in saturating the flue gas plus the amount entrained or combined with the solid waste produced. The remaining liquor (pond or thickener overflow) is recycled to the process. As a result, the chloride concentration can rise to as much as 5,000-10,000 ppm;²⁹ the net result is an extremely corrosive chloride solution. Chloride buildup can also cause a decrease in pH and adversely affect SO₂ removal efficiency. Special corrosion-resistant alloys, which can be expensive, are generally required for service in acidic environments that contain chlorides.

C. Mechanical and Thermal Considerations

While they are being exposed to extremely aggressive acid-chloride solutions, the materials used in FGD systems can be subjected to several sources of erosion and mechanical loading.³⁰⁻³² The reactants used to absorb SO₂ in lime/limestone and magnesium oxide scrubbing systems are insoluble and are introduced as a slurry containing 5-15% solids by weight. Erosion-corrosion can therefore be a problem not only in the recirculation pump and scrubbers, but also in equipment for handling the sludge prior to concentration. Erosion-corrosion can also be produced by fly ash or particulates present in the flue gas prior to their removal. The severity of this type of degradation depends on many variables such as size, concentration, and physical properties of solid particles in the gas or liquid; impinging angle of the particles; flow speed; acid content of the medium; and temperature. In the acid-chloride environment of FGD systems, relatively small mechanical and thermal stresses can lead to stress-corrosion cracking. Fatigue failure is also encountered in the induced-draft (ID) fans.

Flue gas leaving the air-preheater section prior to entering the scrubbing system is cooled to 300°F or less. However, if there is a plant power failure, much hotter gas enters the scrubber system. If the pumps providing quench water to the scrubber system are not provided with emergency power, they too become inoperable. This combination results in temperature excursions in excess of 600°F; under these conditions, organic polymer materials can be destroyed and corrosion in the presence of sulfates and acid chlorides can become more severe.³³ Therefore, it is necessary to incorporate alternative safety features in the design of FGD systems or to choose materials that can withstand these temperature excursions.

D. Current Approaches to Improving FGD Technology

All of the wet scrubbers described above require waste handling, are susceptible to scaling problems, consume large quantities of water and require corrosion-resistant materials for construction. To overcome these difficulties, dry-scrubbing processes have been developed.¹³⁻¹⁵ These processes (Table III) yield a dry waste, eliminating the need for sludge handling. Also, since these systems do not create a corrosive environment, they can be fabricated with inexpensive materials (e.g., low-carbon steel). Although dry systems are attractive from a materials viewpoint, their use is limited to low-sulfur fuels because their SO₂-removal efficiency is lower than that of the wet systems (< 70% vs > 90%). Therefore, the current trend is to update or improve the existing lime/limestone scrubbers by enhancing SO₂-removal efficiency and reducing the amount of sludge produced.³⁴ This is accomplished by the following methods:

- (1) Addition of Mg (thiosorbic lime) to lime or limestone in the scrubber, which produces MgSO₃.
- (2) Addition of adipic acid, which acts as a buffering agent.
- (3) Addition of CaCl₂ and formic acid, which produce CaHSO₃.
- (4) Forced oxidation of CaSO₃ to gypsum, which reduces the amount of sludge, improves the physical properties for disposal purposes, and also produces a useful byproduct.

In all of the above cases, the solution chemistry is altered. For example, the MgSO₃ produced in (1) is more soluble than CaSO₃, and the CaHSO₃ produced in (3) is more soluble than CaSO₃. Both of these process alterations allow a higher concentration of sulfite ions and a higher efficiency of sulfur removal.

IV. SCHEMES FOR SELECTION AND PROTECTION OF WET-SCRUBBER MATERIALS

A. Material Variables and Experimental Conditions

Extensive reports have been written³⁵⁻⁴³ concerning corrosion experience in wet scrubbers, and selection and protection schemes for materials to be used in the highly corrosive scrubber environments. Many of the materials-related problems initially encountered at several plants clearly stemmed from the improper choice of structural materials for the FGD components, which was due in part to the lack of long-term operating experience with a particular material. The material degradation observed (pitting, crevice corrosion, stress-corrosion cracking (SCC), general corrosion, and intergranular corrosion, depending on the location) can be related to corrosion caused by acids and chlorides (present in the liquid, solid or gas phase) and erosion due to abrasive particulates and chemicals utilized in the scrubber systems; cyclic or constant stress can also be a contributing factor. In the case of stainless steel, the chloride attack is often augmented by the scale deposition that invariably occurs in wet-scrubber systems; solids deposited on the surface of the steel decrease the local oxygen supply and help to prevent formation of the protective oxide film. Figure 3 schematically illustrates various types of corrosion⁴⁴ that are possible in FGD systems. Localized attack and fly-ash erosion can occur in spray nozzles where quenching of flue gas takes place. Erosion-corrosion can be a problem with the recirculating pump, while pitting and crevice corrosion can occur in the absorber. Failure of reheater tubes can occur by stress-corrosion cracking. Other areas of concern are dew-point corrosion downstream of the demister and stack, and corrosion-fatigue failure in the ID fans. While Fig. 3 presents a grossly oversimplified picture of the various types of attack, it shows the complexity of the phenomena and highlights the importance of choosing the appropriate materials for each component of FGD systems.

Fig. 3. Wet Scrubbing System, Showing Areas of Possible Corrosive Attack. (Ref. 44)

Some insight into the judicious selection of materials can be obtained from the work of Hoxie and Tuffnell³¹ of International Nickel Co., which is quoted widely in the literature. Their investigations on corrosion of alloys in scrubber environments correlated the extent of localized attack (pitting and crevice corrosion) with (1) chloride-ion concentration and pH of the scrubbing liquor and (2) the molybdenum content of the alloy. Figure 4 shows the effect of pH and chloride content on corrosion of Type 316L stainless steel. The exposure temperatures were generally in the 120-140°F range, but a few were as high as 277°F and one reached 500°F during the upset condition. The combinations of pH and chloride concentration that were tested fell into three regions (severe, sometimes severe, and not severe); severe attack was correlated with low pH and/or high chloride content. Similar results are shown in Fig. 5 for Type 317L stainless steel. The greater resistance of the latter alloy to pitting and crevice corrosion has been attributed to higher Mo content.³¹ The importance of Mo in imparting resistance to chloride attack has been demonstrated by several other investigators,⁴⁵⁻⁴⁹ and is substantiated by the results shown in Fig. 6.³¹ Recently, Crum et al.⁵⁰ have confirmed these results for several alloys in simulated SO₂-scrubber environments (SO₂-saturated solutions containing varying amounts of chlorine). While the latter experiments cannot be directly extrapolated to scrubber environments, they assist in the screening of materials for use in the FGD systems.

Fig. 4. Effect of Chloride Concentration and pH on Rate of Localized Attack on Type 316L Stainless Steel. (Ref. 31)

Fig. 5. Effect of Chloride Concentration and pH on Rate of Localized Attack on Type 317L Stainless Steel. (Ref. 31)

Fig. 6. Effect of Molybdenum Content on Pitting and Crevice Corrosion of Stainless Steels. (Ref. 31)

The type and extent of attack observed for a given material can vary from one location to another in a scrubber assembly. For example, mild steel has experienced severe general corrosion in the inert flue-gas duct; the same material has exhibited pitting in the effluent hold tank and has been completely destroyed by erosion-corrosion below the venturi throat.³³

Stress-corrosion cracking (SCC) has been observed³⁵ in a section of Type 316L stainless steel inlet duct that extends into the cavity above the venturi, at temperatures of 260-330°F and high concentrations (400-8400 ppm) of chloride ion in the process slurry. The residual stresses produced by cold working and welding, as well as the cyclic stresses produced by vibrating equipment, may have contributed to SCC. It is generally known that SCC requires the presence of three factors - surface tensile stress, a susceptible alloy, and a suitable environment. Elimination or alteration of any one of these can prevent attack. In the scrubber environment, SCC can be avoided by proper heat treatment to relieve stresses; however, this is expensive and difficult to carry out for the complete system, and the usual solution is to select special corrosion-resistant alloys.

The use of acid-chloride resistant alloys for FGD components can be prohibitively expensive because of the large number of components affected. This can be illustrated by considering the scrubber system above the demister, where there is no circulation of the scrubbing liquid. Extensive corrosion, caused by the accumulation of acids and solids, can occur in the demister, induced-draft blades, duct, separator-tower top cone, fan inlet box, reheater tubes, and stacks. In many cases, the first corrosion failure occurs in the region after the demister. Fans downstream of the scrubber appear to be particularly prone to corrosion because the heat they generate dries out the scrubbing liquid, allowing acids, chlorides, and other solids to accumulate. In addition, the fan head is subjected to significant rotational and vibrational stress and is hence susceptible to SCC and corrosion fatigue. Type 316L stainless steel has a relatively low yield point, thus limiting the fan lifetime. Materials such as Inconel 625 or Hastelloy C have better mechanical properties as well as corrosion resistance, but are expensive. Stack material is subjected to acid and chloride condensates; because of the large amount of material required in the stack, the use of corrosion-resistant alloys is very expensive. Thus, other approaches to solving corrosion problems, such as the use of organic and inorganic materials and linings on inexpensive alloys such as mild steel, must be considered. The low-temperature environment prevalent in scrubber systems permits the use of these materials in connecting ducts, scrubber body, fan housings, stacks, and many other FGD components.

As we have discussed, most of the FGD components undergo some form of corrosion, although the severity and form of corrosion can significantly vary from one location to another. The choice of materials of construction (alloys, organic and inorganic materials, linings) should be based on several environmental factors discussed in previous sections of this report, such as composition of the gas streams and scrubber liquor, pH of influent and effluent liquor, temperature of scrubbing liquor and exhaust gases, velocity of liquor and gas streams, and abrasiveness of particulates in gas and liquid. Material selection and protection schemes are also affected by cost

considerations and operating procedures, and can thus vary from one plant to another.

B. Materials Used in Current FGD Systems and Their Performance

From the preceding discussion, it is clear that no single material seems universally acceptable for SO₂ scrubbers from the viewpoints of both performance and cost. Several investigators³⁵⁻⁴¹ have discussed the choice of materials for wet flue-gas scrubbers and experience related to corrosion and other processes that lead to materials degradation. The most extensive survey of FGD systems and operating experience with respect to materials performance has been carried out by Rosenberg et al.,²² who reviewed ~40 systems (see Table IV). Also of great value are the continuing EPA surveys of FGD processes used by utility companies (see, for example, Refs. 51 and 52). These surveys cover operating experiences at existing plants and include flow diagrams of all operating scrubbers. In addition, information is given on plants under construction, thus providing guidance as to which problems are likely to be most important in the future.

The materials utilized in FGD systems in operation today fall into three categories: (1) alloys, (2) ceramic and inorganic materials, and (3) organic materials. Some of the important alloys of current interest are listed in Table V. Depending upon the application, the alloys are either unprotected or protected with thick organic coatings or ceramic material. The coatings are sometimes impregnated with alumina to improve abrasion resistance. Organic linings find applications in prescrubbers, absorbers, ducts, stacks and tanks. Inorganic materials are sometimes used for prescrubbers, spray nozzles, slurry pumps, outlet ducts, bypass ducts, and stacks. Pre-fired acid- and wear-resistant bricks, sometimes reinforced with chemically bonded materials (silicon aggregates, sodium silicate, silicon fluoride and colloidal silica bond phase) are used as prescrubber, outlet-duct, and stack linings. The following brief summary of materials used for FGD components (details can be found in Ref. 22) shows the flexibility that exists in the choice of materials for specific components:

Prescrubbers: These are chambers through which the flue gas passes with little SO₂ removal. Because hot erosive conditions prevail, organic coatings or linings on carbon and alloy steels are not very useful unless they are protected with another material such as hydraulic or chemically bonded concrete. Alloy steels without linings are also used. Since Types 304 and 316L stainless are susceptible to chloride attack, the current trend is to choose 317L, Uddeholm 904, Incoloy 825, or Inconel 625.

Absorbers: A combination of materials such as alloy steels, rubber-lined and other organic-lined carbon steel, and ceramic-lined carbon steel is used.

Spray Nozzles: Many materials, ranging from plastic (Noryl resin) to extremely hard alumina (Al₂O₃) and silicon carbide (SiC), are used.

Mist Eliminators: All are chevron-type, with a variety of vane shapes. The vanes are made of plastic, with or without fiberglass reinforcement. Among alloys used for this component, Type 316L stainless steel is a common choice, although Hastelloy G is better.

Table IV. Description of FGD Systems Visited (Ref. 22)

Utility and Plant	Size in MW	Wt. % Sul- fur in Coal	FGD Vendor	Reagent for SO ₂ Removal	Method of Particulate Removal	Type of SO ₂ Absorber	Number of Absorber Modules	Bypass Capability	Type of Stack Gas Heated	Method of Waste Disposal	Start-Up Date
Alabama Electric Corp Tombigbee 2	255	1.5-1.8	Peabody	Limestone	ESP	Spray tower	2	Yes	Bypass	Pond; open loop	9/78
Tombigbee 3	255	1.5-1.8	Peabody	Limestone	ESP	Spray tower	2	Yes	Bypass	Pond; open loop	6/79
Ariz. Elec. Power Corp Apache 2	195	0.4-0.5	B-C	Limestone	Hot ESP	Packed tower	2	Yes	Bypass	Pond; open loop	2/79
Apache 3	195	0.4-0.5	B-C	Limestone	Hot ESP	Packed tower	2	Yes	Bypass	Pond; open loop	6/79
Arizona Public Service Cholla 1	115	0.4-0.6	B-C	Limestone	Multistage & FDS	Packed tower	2	Yes	In-line steam coils	Pond; open loop	12/71
Cholla 2	265	0.4-0.6	B-C	Limestone	Multistage & FDS	Packed tower	4	Yes	In-line steam coils	Pond; open loop	5/78
Central Illinois Light Buch Creek	400	3.4	B/E	Limestone	ESP	Venturi-Sorber ^(a)	4	Yes	None	Pond; closed loop	7/76 & 7/78 ^(a)
C & S Ohio Electric Conneville 5	410	4.5	UOP	Thiosorbic lime	ESP	One-stage TCA	2	Yes	None	Landfill; closed loop	1 & 11/77
Conneville 6	410	4.5	UOP	Thiosorbic lime	ESP	One-stage TCA	2	Yes	None	Landfill; closed loop	4/78
Commonwealth Edison Mill Creek 1	167	0.5-4.0	BM	Limestone	Venturi	Tray tower	2	Yes	In-line steam coils	Landfill; closed loop	7/73
Dequette Light Elmore	494	2.0	Chasico	Thiosorbic lime	ESP & venturi	Venturi	5	No	None ^(b)	Landfill; open loop	10/75
Phillips	387	2.3	Chasico	Thiosorbic lime	ESP & venturi	Venturi	6	No ^(c)	None ^(b)	Landfill; open loop	7/73
Indianapolis P & L Petersburg 3	515	3.0-4.5	UOP	Limestone	ESP	Three-stage TCA	4	Yes	Indirect hot air	Landfill; closed loop	12/77
Kansas City P & L Bouthorn 3	100	4.0	CE	Lime ^(d)	One-stage marble bed	One-stage marble bed	2	Yes	In-line hot water tubes	Pond; open loop	11/72
Bouthorn 4	100	4.0	CE	Lime ^(d)	One-stage marble bed	One-stage marble bed	2	Yes	In-line hot water tubes	Pond; open loop	8/72
La Crosse 1	870	5.4	BM	Limestone	Venturi	Two-stage tray tower	8	No	In-line steam coils	Pond; open loop	6/73
Kansas Power & Light Lawrence 4 (old)	125	3.3-4.0	CE	Limestone ^(e)	One-stage marble bed	One-stage marble bed	2	Yes	In-line hot water tubes	Pond; closed loop	10/68
Lawrence 4 (new)	125	0.9	CE	Limestone	Red venturi	Spray tower	2	Yes	In-line hot water tubes	Pond; closed loop	1/77
Lawrence 5 (old)	400	3.3-4.0	CE	Limestone ^(e)	One-stage marble bed	One-stage marble bed	8	Yes	In-line hot water tubes	Pond; closed loop	9/71
Lawrence 5 (new)	400	0.9	CE	Limestone	Red venturi	Spray tower	2	Yes	In-line hot water tubes	Pond; closed loop	4/78
Kentucky Utilities Crown River	52	3.5-4.0	AAP	Lime	Venturi	Mobile bed	1	Yes	None	Pond; closed loop	9/75

Table IV. (Continued)

Utility and Plant	Size in MW	Wt. % Sul- fur in Coal	PCB Vendor	Reagent for SO ₂ Removal	Method of Particulate Removal	Type of SO ₂ Absorber	Number of Absorber Modules	Bypass Capability	Type of Stack Gas Reheat	Method of Waste Disposal	Start-Up Date
Louisville G & E											
Coal Run 4	178	3.9	AAP	Carbide lime	ESP	Mobile bed	2	Yes	Fuel-oil fired	Pond; open loop	8/76
Coal Run 5	190	3.8	CE	Carbide lime	ESP	Spray tower	2	Yes	In-line steam coils	Pond; open loop	12/77
Hill Creek 3	425	3.9	AAP	Carbide lime	ESP	Mobile bed	4	Yes	In-line steam coils (f)	Pond; open loop	7/78
Paddy Run 6	85	3.7	CE	Carbide lime	ESP	Two-stage marble bed	2	Yes	Natural gas burners	Landfill; closed loop	4/75
Minnesota Power Corp Milton N. Young 2	440	0.7	CEA	Alkaline fly ash	ESP	Spray tower	2	Yes	Bypass	Landfill; closed loop	5/77
Montana Power Colstrip 1	360	0.7	CEA	Lime/alka- line fly ash	Venturi	Venturi and spray zone	3	No	In-line steam coils	Pond; closed loop	11/75
Colstrip 2	360	0.7	CEA	Lime/alka- line fly ash	Venturi	Venturi and spray zone	3	No	In-line steam coils	Pond; closed loop	8/76
Northern States Power Shurtleff 1	720	0.8	CE	Limestone/alka- line fly ash	Rob venturi	One-stage marble bed	12	No	In-line hot water tubes	Pond; open loop	5/76
Shurtleff 2	720	0.8	CE	Limestone/alka- line fly ash	Rob venturi	One-stage marble bed	12	No	In-line hot water tubes	Pond; open loop	4/77
Pennsylvania Power Bruce Mansfield 1	825	2.0-5.0	Chemico	Thiosorbic lime	Venturi	Venturi	6	No	None (b)	Pond; open loop	4/76
Bruce Mansfield 2	825	2.0-5.0	Chemico	Thiosorbic lime	Venturi	Venturi	6	No	None (b)	Pond; open loop	10/77
S. Carolina Pub. Serv. Wayah 2	280 (a)	1.0	BAU	Limestone	ESP	Venturi & one stage tray tower	1	Yes	Bypass (b)	Pond; open loop	8/77
S. Mine. Elec. Power R. D. Morrow 1	200	1.6	R/E	Limestone	ESP	Venturi-Sorber (c)	1	Yes	Bypass	Landfill; closed loop	9/78
R. D. Morrow 2	200	1.6	R/E	Limestone	ESP	Venturi-Sorber (c)	1	Yes	Bypass	Landfill; closed loop	6/79
S. Ill. Power Corp Mazon 4	184	< 3.5	BAU	Limestone	ESP	Two-stage tray tower	2	Yes	None	Landfill; closed loop	4/79
Springfield City Util. Southwest 1	194	3.5-4.0	UOP	Limestone	ESP	Three-stage TCA	2	Yes	None	Landfill; closed loop	4/77
TVA Widow Creek 6	550	4.0	TVA	Limestone	Venturi	Tray tower	4	Yes	Indirect hot air	Pond; closed loop	5/77
Utah Power & Light Burlington 1	432	0.6	Chemico	Lime	ESP	Spray tower	4	Yes	Bypass & indirect hot air	Landfill; closed loop	5/78

(a) One module started up in July, 1976 and operated intermittently until March, 1977; all four modules started up in July, 1978.

(b) Oil-fired reheaters were installed but never used because of operating problems.

(c) The FGD system can be bypassed, but shutdown of the boilers is necessary to divert the flow.

(d) Converted from limestone injection into boiler to tail-end lime scrubbing.

(e) Limestone injection into boiler.

(f) Not yet installed.

(g) Only half of the flue gas is scrubbed.

(h) Blended in stack; scrubbed gas enters about 100 ft above bypass breeching.

Table V. Major Alloys Currently in Use or Planned for Use in FGD Components

	Typical Composition (wt.%)					
	Cr	Mo	Ni	Fe	C	Other
<i>Iron-base Alloys</i>						
Carbon Steel	-	-	-	Bal	0.20 (max)	-
316L	17	2.5	12	Bal	0.03	
317L	19	3.5	13	Bal	0.03	-
Uddeholm 904L	20	4.5	25	Bal	0.02	-
<i>Nickel-base Alloys</i>						
Incoloy 825	21.50	2.99	Bal	30.29	0.04	1.94 Cu, 0.73 Mn, 0.32 Si, 0.67 Ti, 0.04 Al, 0.007 S
Hastelloy G	21.4	6.7	Bal	18.50	0.03	1.38 Mn, 1.74 Cu, 0.69 Si, 0.0005 S, 0.014 P, 2.00 Co, 0.356 S, 2.31 Nb
Inconel 625 ^a	21.96	8.98	Bal	2.97	0.06	0.17 Mn, 0.33 Si, 0.34 Ti, 0.14 Al, 0.003 S, 0.008 P, 3.62 Nb + Ta

^aTitanium (commercial grade) can substitute for this alloy.

Reheaters: Materials of construction range from carbon steel to Inconel 625 and Incoloy 825 alloys. For low-sulfur coal, Type 316L stainless steel can also be used. Fan housings are rubber lined.

Ducts: Inlet ducts are made from carbon steel or Cor-Ten steel, with Type 316L stainless steel used for some parts. Outlet-duct materials range from unlined carbon steel to Hastelloy G and Inconel 625. In wet outlet-duct sections, organic linings (commonly polyester or epoxy with flake reinforcement) are used to protect the carbon steel structure.

Expansion Joints: The expansion joints in the scrubber system are made of an elastomer with fabric. Fiberglass, asbestos, and metal expansion joints are also in use.

Dampers: Inlet dampers use unlined carbon steel; the damper seals are made of alloys such as Type 316L or 317L stainless steel, Hastelloy G, or Inconel 625. The current trend is to replace 316L by Uddeholm 904L frame, Inconel 625 seals, and Hastelloy C fasteners.

Stacks: Acid-resistant brick, inorganic and hydraulic cement-bonded concrete, and fluoroelastomer linings have replaced organic linings. High-nickel alloys are being considered.

Storage Silos: Unlined carbon steel is satisfactory, as it is exposed only to alkaline conditions.

Grinding Mills or Slakers: Carbon steel with or without Ni-hard and rubber linings is used.

Pumps: Pumps are fabricated from carbon steel (lined or unlined). The lining, if used, is usually of rubber. Problems with unlined Carpenter 20 steel pumps have been solved by using impellers fabricated of 317L, Ti, and Fe-20%Cr alloys. Silicon carbide wear plates, epoxy bonded to steel, are used for housings.

Pipings and Valves: Rubber-lined carbon steel, fiberglass-reinforced plastic (FRP), and Types 316L and 317L stainless steel alloys are commonly used.

Tanks: Unlined carbon, concrete, FRP, 316L, and carbon steel with some form of glass flake-filled polyester lining are utilized in the construction of tanks.

Agitators and Rakes: Blades are constructed of rubber-clad carbon steel, and shafts of stainless steel and unlined carbon steel.

Vacuum Filters and Centrifuges: The vacuum filters and centrifuges used for sludge dewatering are made of carbon steel with or without organic linings, and the filter cloth is prepared from either polypropylene or nylon.

From the above description of the materials for the FGD components, it is clear that there is a great deal of choice and flexibility with regard to the materials of construction. Hence, it is no surprise that satisfactory

operation for as long as 2-8 years has been reported²² for a few of the FGD components. The operating experience varies from plant to plant; however, an assessment²² of the materials problems encountered in a number of FGD systems shows that most of the components have a history of materials problems ranging from minor to significant and prolonged. In general, the materials performance in the existing plants has been better for the components located within the scrubber than for the components located downstream of the scrubber. Because of the varying experience and the uncertainty in the characterization of environments, it is not possible to establish the statistical significance of failures. Also, for many of the materials of current interest in FGD systems, particularly organic liners for carbon steel components and organic and inorganic liners (bricks, refractories, fiber-reinforced plastic, etc.) for stacks, performance limits have not been established.

Also, a closer examination of Table IV and Fig. 7 shows that the experience for the larger (> 400-MW) FGD systems which employ closed-loop operations, where higher concentrations of chloride can occur with time, is rather limited (shaded area in Fig. 7). Although Incoloy 825 and Inconel 625 have shown better corrosion resistance than austenitic stainless steels in SO₂-scrubbing environments, some corrosion has occurred (Figs. 8 and 9), which can be significant over the anticipated 30-year life span of the FGD systems. The data⁵³ in Figs. 8 and 9, which were collected from thirty different plant locations that included utilities, industrial power plants, and copper smelters, also show that Inconel 625 is superior to Incoloy 825 in FGD environments. Unfortunately, the use of these alloys in bulk quantities for SO₂-removal systems is expensive, and their performance over longer periods of time (> 5 years) remains to be demonstrated. These considerations of cost and unknown long-term performance may lead to a search for alternate materials based on experience and research studies.

Fig. 7. Wet Scrubbers for Which Operating Experience is Available.

Fig. 8. Effect of Chloride Concentration and pH on Pitting Rate of Incoloy 825. (Ref. 53)

Fig. 9. Effect of Chloride Concentration and pH on Pitting Rate of Inconel 625. (Ref. 53)

For the installation of future lime/limestone systems, a better selection of materials may become possible. However, this alone will not solve such problems as sludge disposal, which has been described elsewhere.⁵⁴ For example, for a 500-MW boiler plant burning 3%-sulfur coal, 500,000 tons/yr of sludge will be generated at 50% solids. The sludge consists primarily of $\text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 or $\text{Ca}(\text{OH})_2$, and fly ash. It is thixotropic and has the consistency of toothpaste or heavy mud. The usual method of disposal, to a pond situated at or adjacent to the plant site, requires many acres of land which will eventually become filled. To deal with this land wastage problem, chemical fixation processes are being developed whereby the sludge is converted to a solid product which is either usable or easily disposed of. As a result of dewatering of the sludge, chloride buildup in the scrubber system will further enhance the susceptibility to corrosion unless appropriate measures are taken in the selection of materials.

V. SUMMARY AND CONCLUSIONS

The chemistry and parameters of the flue-gas desulfurization (FGD) process are discussed for lime/limestone and other scrubber systems. The environments to which the structural materials are exposed are characterized in terms of variables pertinent to process chemistry, such as pH and chloride content, as well as mechanical and thermal variables. Even under normal operating conditions, the environments are highly corrosive. In systems involving closed-loop operations, the chloride concentrations in the water may exceed 10,000 ppm and thus the environment continually becomes more corrosive. Consequently, FGD systems require either corrosion-resistant materials (e.g., Inconel 625, Incoloy 825), which are normally used for high-temperature applications, or less expensive materials such as carbon steel with organic coatings (e.g., rubber linings, epoxy). The use of conventional alloys and the selection of alternate materials (alloys, ceramics, other inorganic and organic materials) for the FGD components are briefly described in this report. A critical evaluation of the materials currently in use for many FGD components (mostly those of lime/limestone systems), as judged from their performance over a period as long as 2-8 years, shows that materials problems vary from one FGD plant to another and from one location to another within an FGD plant. Materials research should be conducted for components that have a significant and prolonged history of materials problems and that force a plant shutdown when they fail. In general, the materials problems relative to corrosion appear to be more pronounced and critical for components located downstream of the scrubber than within the scrubber. In light of these existing problems, it is important to examine areas where research and evaluation could significantly contribute to the proper selection of materials.

VI. RECOMMENDATIONS

The utility companies and other private industries that burn coal have faced considerable economic penalties in installing FGD scrubbing systems to meet the EPA emission standards. In fact, the costs of flue-gas scrubbers are estimated to be 25-30% of the total fossil utility plant investment. This cost may run even higher if more stringent controls are placed on air pollution in the future. It is also clear that many components of the existing FGD systems (e.g., stack linings, ducts, bypass-duct junctions, and reheaters) have a history of materials-related failures, many of which require complete shutdown of the plant. Therefore, materials selection is becoming increasingly important as financial pressures are felt by the utility companies. Proper selection of materials of construction through an appropriate research and development plan can be expected to have great economic impact on current FGD technology. It is a vital aspect in both the design of new FGD facilities and the improvement of existing facilities. It is recommended that a program be undertaken which emphasizes (a) failure analysis of FGD components and (b) materials research and evaluation by means of both controlled laboratory tests and field studies.

A. Failure Analysis

The continuing EPA surveys of utility companies with existing FGD installations include detailed records on operating experience at these plants. Although useful, this alone is not sufficient to alleviate the problems that are encountered, as the environments in which failures are occurring are not well characterized in many cases. A rigorous analysis of failures occurring in various FGD environments should be undertaken to establish the environmental and statistical significance of failures and, wherever possible, to correlate failures with the service environment. This is necessary to identify the areas of materials research that will have the greatest potential economic impact on the plant. It is important to establish whether the failures are site-specific, e.g., related to the coal, water, or chemicals used in the process, or associated with an improper choice of materials or with a design variable.

B. Research on Materials

As discussed in this report, the available data on performance of materials in various FGD systems have provided some direction for future efforts. It has been clearly demonstrated that neither austenitic stainless steel nor uncoated carbon steel meets the criteria of long life and trouble-free service with a minimum of expensive maintenance requirements. More corrosion-resistant alloys, such as Inconel 625 and Incoloy 825, have demonstrated better performance, although their long-term (>5 yr) reliability in service remains to be seen. Materials research on these alloys would be useful, but more economic benefit would be realized if less expensive alloys such as carbon steel, coated with one of these corrosion-resistant alloys or with organic materials, could be substituted. A number of new coating procedures aimed at cost savings are currently available, and the applicability of this technology to FGD environments should be investigated. The substitution of other, less expensive, corrosion-resistant high-grade metal systems and alloys (e.g., Ti) should also be explored. In summary, future studies

in the following materials areas would be of interest and value from an economic viewpoint:

- (1) Organic coatings on inexpensive alloys such as carbon steel.
- (2) Coatings of (expensive) corrosion-resistant alloys, such as Inconel 625, on inexpensive alloys.
- (3) Fiber-reinforced plastics and/or refractory materials for stack linings.
- (4) Less expensive, corrosion-resistant high-grade metal systems (e.g., Ti) and alloys.
- (5) Inexpensive alloys for which surface compositions can be modified to enhance their corrosion resistance in FGD environments.

1. Controlled Laboratory Experiments

The erosion-corrosion problems encountered in FGD environments are varied in nature and depend on a large number of factors; in many cases, FGD processes are not well characterized in terms of the environmental variables (e.g., pH, chloride content). Therefore laboratory experiments alone may prove insufficient to predict material behavior. However, laboratory studies are invaluable in narrowing the list of candidate materials that need to be tested under actual operating conditions.

Laboratory experiments similar to those already done on high-nickel alloys⁵⁰ and stainless steels are needed to evaluate the effects of variables such as pH, chloride content, and temperature on coated and uncoated materials. For uncoated materials, these experiments yield information on weight loss (corrosion rate), pitting rate, and type of attack. But organic coatings do not exhibit the same responses as metals in corrosive service. The dimensions of these coatings are rarely changed by exposure to corrosive media; rather, the effect of the FGD environment, if any, may be to alter the structure of the coatings at varying rates. This can lead to decohesion and eventual mechanical failure of the coating material. Thus, study of the rates at which coating properties change should shed light on the reliability of the material. The abrasive resistance of some of the coatings on steels can be determined in accordance with ASTM standards. It is also necessary to develop testing methods to evaluate the mechanical and thermal stability of stack linings prior to application.

2. In-service Testing

Since the types of corrosion failures observed in FGD systems are numerous, it is important to investigate a variety of different types of failures, such as crevice corrosion and susceptibility to SCC, in material systems being considered for FGD applications. In-service testing using small specimens and actual or simulated components is extremely important to

characterize the synergistic effects of chemical and design variables as well as to test the validity of FGD design practice. The field tests should be carried out in the best-characterized FGD environments. Post-testing of materials is an important part of the proposed program, as it helps to identify the failure mechanisms, performance limitations and potential problem areas.

VII. MATERIALS PROGRAM FOR LIME/LIMESTONE SCRUBBER COMPONENTS

A. Scope

The proposed Argonne National Laboratory (ANL) program will provide materials support for wet scrubbers with particular emphasis on lime/limestone scrubber technology. The objective of the program is to evaluate materials capability for existing scrubbers as well as guide materials selection for future processes and developments. The overall program comprises three subtasks:

- (1) Failure analysis of field components.
- (2) Materials testing and evaluation.
- (3) Analysis and recommendations.

Comprehensive failure analyses are needed to identify the underlying mechanisms of actual field failures. The results will have an immediate impact on the repair and reliable operation of scrubber systems, and will provide guidance for the selection of materials for additional testing and evaluation. Systematic laboratory and field testing are needed to develop adequate information for the selection and development of improved materials. In addition to the data obtained, the impact on the overall process economics and reliability will be taken into account in making specific recommendations concerning materials selection. The results will be documented in the form of quarterly reports and an interim report at the end of each year; a final report will be issued on completion of the program.

Based on our evaluation of materials performance in existing lime/limestone scrubbers, we have chosen to concentrate on problems related to critical components, namely stacks, ducts (downstream), and reheaters. However, in the future, if critical problems develop in other components (e.g., erosion in ID fans) as a result of continued operation of the existing plants and process developments, we will redirect the program accordingly.

Throughout this program, close contact will be maintained with the utility companies and equipment manufacturing companies so that the information generated by the program can be made available to guide decisions on repair or replacement of scrubber components, improved operation of existing plants, and materials selection in the construction of new scrubbers.

The scope of the proposed program must, of course, be compatible with the available funding. The test variables involved are complex and the materials utilized in the scrubbers are numerous, ranging from plastic to iron- and nickel-base alloys. The proposed program includes field tests on specimens in service and removal of the specimens for evaluation at specified intervals. Tests made under actual operating conditions in plants can be expected to provide reliable guidelines for the selection of materials to be used under similar conditions. These tests may be supported by supplementary tests using controlled conditions.

For the first year, the proposed budget is about \$250 K, which is expected to fund 1 staff member, 1.5 support personnel, and capital equipment including environmental chambers. In the first year, our efforts will be directed primarily toward the development of testing facilities, specimen design and preparation, and interaction with the utility companies concerning field tests and failure analysis. Further development of testing capabilities will be required as the program continues. Some exploratory and feasibility experiments will be performed as testing equipment becomes available. We recommend that the program be expanded after the first year to provide 1 staff member and 1.5 support personnel for the materials evaluation program (which includes both laboratory and field experiments) and additional staff and support personnel (0.5 man-year each) to perform failure analyses and other tasks. Since the current investment in scrubbers forms a significant fraction of the total plant cost and the availability and reliability of existing scrubbers (especially those associated with high-sulfur coal) are unsatisfactory, we believe that the proposed materials program is the minimum necessary to provide adequate materials support for scrubber technology.

B. Proposed Program

1. *Failure Analysis of Field Components*

Failure analysis is an important part of the materials program. It provides information on material performance under actual operating conditions. The results will have an immediate impact on the repair and reliable operation of scrubber systems. Furthermore, they will provide valuable information and guidance for the materials evaluation program as well as for the selection and development of materials for future plants.

It is not feasible or informative to investigate all the failures encountered in the scrubber assemblies, and therefore, we propose to focus primarily on those failures which result in a complete plant shutdown, e.g., failure of stacks or downstream ducts. In addition to these critical components, reheaters and fans represent particularly trouble-prone components where further materials development and improvement can be beneficial, and therefore will be included in the program. To determine the failure cases to be examined, it is necessary to work closely with the utility companies and to utilize other sources of information such as the EPA utility FGD survey. A failure analysis will generally begin with plant trips to acquire detailed information concerning the design, fabrication, and service history of the failed components and to select components for detailed investigation. A complete analysis could involve, for example, metallographic and other microstructural examinations; the use of other analytical tools, such as

x-ray spectroscopy; mechanical testing; and thermal and stress analysis. If necessary, the expertise of other ANL staff in the areas of general corrosion, intergranular corrosion, stress-corrosion cracking, and corrosion fatigue is available on a case-by-case basis. We will also interact with utility companies to take advantage of their experience and to confirm our findings. A detailed report of our findings will be issued together with our recommendations for future action. The ANL effort will be coordinated with that of other DOE contractors to avoid duplication.

2. Materials Testing and Evaluation

The materials evaluation program will be coordinated with the failure analysis efforts, and therefore, it will primarily be concerned with the same components, namely stacks, downstream ducts, reheaters, and fans. At present, these components are fabricated from a variety of materials, as discussed in Chapter IV of this report. Therefore, a judicious choice of materials to be tested is important to insure the development of a meaningful program. The initial selection of materials for the proposed program is based on the available experience related to materials performance of wet scrubbers, as discussed in this report, and includes consideration of process modifications and requirements for future processes.

During service, materials in the scrubber will experience a combination of complex chemical, thermal, and stress environments. For example, in reheaters, residual stresses exist in the welds and thermal stresses are produced as a result of fluctuations in temperature of the steam, hot water, and flue gas. Acid and chloride condensates on the surfaces of various components produce aggressive chemical environments. The chemical composition of these deposits can vary as a function of time in a plant, depending on the operating conditions and the impurity content of the coal, water, and lime/limestone utilized in the process. Particularly for the scrubbers that operate in a closed-loop mode, the amount of chloride buildup increases with time, producing a continuously changing corrosive environment. In addition, the scrubber components (e.g., ducts and stacks) experience alternate periods of "dry" and "wet" conditions in conjunction with temperature fluctuations.

It is well known⁵⁵ that the rate of degradation of materials is more rapid under cyclic conditions than under conditions of exposure in a steady-state situation. The material degradation is augmented by cyclic loading and temperature cycling, and furthermore, the existence of cyclic "dry" and "wet" states results in the enhancement of corrosion rates. Therefore, the effects of cyclic environmental variables on the degradation rate of scrubber materials must be emphasized in the proposed program. It is also possible that combinations of more than one type of cyclic effect may exist, depending on the system. It should be recognized that it is difficult to define "typical" operating conditions for the existing plants, which undergo frequent and lengthy shutdowns, such that environmental variables are not well characterized. Hence, it is essential to develop a program that includes both laboratory and field experiments.

The proposed program includes laboratory corrosion tests under dynamic conditions and under a combination of one or more environmental cycling variables (e.g., temperature, pH, stress, and chlorine), and corrosion fatigue tests. Because tests under cyclic conditions are more difficult and expensive, simpler tests with constant environments and constant mechanical loads will be used first as screening tests to identify the most promising materials for more comprehensive testing. Thus, the testing program will include three general types of laboratory experiments:

(a) Laboratory exposure under steady-state conditions with controlled temperature, chemistry, and stress. For metallic specimens, the depth of corrosive attack and related microstructural changes and the number, depth, and distribution of pits, cracks, etc. will be examined. For non-metallic specimens, visual and microstructural examinations will be made and the dimensional changes, elastic modulus, strength, hardness, and other variable properties determined.

(b) Laboratory exposure under cyclic environmental conditions. In this type of experiment, the chemistry and temperature of the corrosive environments are controlled such that the specimen is subjected to cycling of temperature and/or chemical environment at various frequencies. After the exposure, specimens are examined in the same fashion as in (a) to determine the extent of degradation involved. Other experiments will involve cycling between "dry" and "wet" conditions, which is expected to be especially important for plastics.

(c) Stress and strain cycling of specimens in corrosive environments. A limited number of fatigue tests under controlled temperature and chemical environments will be performed to evaluate the material response to cyclic stress or strain cycles. Corrosion fatigue tests, while recognized as important for metals, have not been widely used for plastics. Both post-exposure and in-situ experiments will be considered. Thus, these experiments, in addition to providing a design data base for the materials, are expected to develop into a standard testing procedure for evaluating the response of materials to the hostile environments of scrubber systems. Changes in flexural modulus and strength have been the principal parameters used to date for estimating the degradation of the chemical resistance of plastics in a corrosive environment. It is hoped that corrosion fatigue tests under more realistic testing conditions will provide additional quantitative information to supplement the present practice. The methods of corrosion data correlation are well established for metallic materials and the test results will be applicable to stacks, ducts, reheaters, and ID fans. The data obtained will be in the form of cycles to failure or crack initiation and growth rates as a function of temperature, stress, and chemical environments.

In the field experiments, specimens will be exposed to corrosive environments at critical locations in the outlet ducts, reheater, and stacks to simulate the response of components to scrubber environments. The specimens will be removed after various exposure times and the extent of material degradation evaluated in a manner similar to that used for the laboratory specimens.

The plan outlined in Table VI shows the number of specimens that can be tested over a five-year period based on the proposed funding level. For a specific material such as FRP, approximately 10 specimens can be tested and examined per year for a given set of experimental conditions. To illustrate the extent to which the range of test variables and materials can be investigated, we consider 5 cycling parameters of interest (narrow and broad temperature ranges, stress range, pH range, and chlorine range) and 4 non-cycling steady-state variables (temperature, 72-350°F; pH, 1-6; chlorine, 10^2 - 10^5 ppm; and stress) in the materials evaluation program. For a given material, the number of tests needed to assess all the above variables is ~80. Thus, we will be able to examine only a limited number of materials, e.g., one metallic system, one FRP, and one lined or coated material.

Careful consideration will be given to the results of the initial screening tests and prior field experience before the materials for more intensive testing are selected. The screening tests will also be used to rank the test variables and estimate their importance. However, even if only half of the variables listed above prove to be important, the capability for in-depth investigation still appears to be limited to only a few materials.

3. Analysis and Recommendations

As pointed out earlier in this chapter, our recommendations on the materials evaluation and performance limits will be documented in an interim report at the end of each year along with a final report after the completion of the program. The recommendations will be based on the findings of our laboratory and field studies, information available in the literature, and the results of other DOE contractors. In the analysis, data on materials properties as well as evaluation of present and future processing variables and economic factors will be considered so as to optimize the materials selection and maximize the performance of the scrubber systems. Throughout the program, we propose to interface with utility companies and other DOE contractors so that we can share our findings and experience. This type of interaction is especially important in the decision-making process concerning repairs, replacement and construction of scrubber systems, and also in the screening of materials of construction for the systems. It is recognized that many of the materials of construction for scrubbers, particularly coatings, may vary in quality from one manufacturer to another depending on the method of application and surface preparation. It is therefore important to develop a useful and efficient quality assurance program to ensure successful field performance. The proposed ANL program will provide information needed to establish the required test procedures for materials prior to their use in scrubbers.

Table VI. Approximate Number of Laboratory and Field Tests That Can Be Performed on Various Materials Over a Five-year Period with the Assumed Man-Year Support Level^a

Material & Relevant Components	Type of Test	Year				
		1	2	3	4	5
Metallic System (e.g., Inconel 625) Reheater	Corrosion in flowing liquid	5 (10) ^b	10	10	10	10
	Temperature/environmental variable cycling	2	10	10	10	10
	Corrosion fatigue		<5	<5	<5	<5
	Field test	Specimen preparation and installation	10	10	10	10
Metallic System (e.g., Ti, ferritic steels) Duct and stack	Field test	Specimen preparation and installation	10	10	10	10
Plastic (e.g., FRP) Duct and stack	Corrosion in flowing liquid	5 (10)	10	10	10	10
	Temperature/environmental cycling	2	10	10	10	10
	Corrosion fatigue		<5	<5	<5	<5
	Field test	Specimen preparation and installation	10	10	10	10
Linings for carbon steel (e.g., rubber, epoxy, FRP) Duct and stack	Corrosion in flowing liquid	5 (10)	10	10	10	10
	Temperature/environmental cycling	2	10	10	10	10
	Corrosion fatigue		<5	<5	<5	<5
	Field test	Specimen preparation and installation	10	10	10	10

^a1.5 staff + 2 support personnel after the first year.

^bNumbers in () indicate screening tests in addition to exploratory tests.

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