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EVALUATION OF LIME/LIMESTONE SLUDGE DISPOSAL OPTIONS



U.S. ENVIRONMENTAL PROTECTION AGENCY

Office of Air and Water Programs
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

EVALUATION OF LIME/LIMESTONE SLUDGE DISPOSAL OPTIONS

by

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ABSTRACT

The report presents results of a study of technology for disposal of sludge created by lime and limestone flue gas desulfurization systems at steam-electric power plants. Effects of operating variables on the volume of sludge produced are explained with emphasis on plant situations in the State of Ohio. Properties of sludges are reviewed, including settling characteristics, rewatering tendency, strength, particle size, bulk density and chemical composition. The report considers potential environmental hazards of sludge disposal, namely contamination of water and ground water supplies. Methods of avoiding these hazards are presented and evaluated. Technologies for solidifying (fixating) sludge are discussed and evaluated along with the current status of full-scale projects. The report concludes that any large degree of commercial utilization is unlikely. available data, there are no insurmountable technological problems in disposing of sludge in an environmentally acceptable manner. While economics of disposal are not well-defined, studies are underway that should provide better cost information and other valuable information.

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SUMMARY

One of the major problems inherent in any flue gas desulfurization system is the necessity to dispose of or utilize large quantities of sulfur removed from the flue gas. The sulfur compounds produced by flue gas desulfurization systems fall into two general categories: throwaway or saleable products. Lime/limestone scrubbing systems generate a throwaway sludge with little commercial value at the present time.

The environmental effects of sludge disposal will be dictated by the chemical and physical properties of the material, and these properties may vary widely for different operations. One potential environmental effect of considerable concern is water pollution, both surface water and groundwater, and it is the chemical properties of the sludge which are relevant to this area. Another environmental concern is land reclamation of disposal sites, and it is the physical properties of the sludge which are most relevant to this area. With proper site selection and design, including a permanent impermeable liner, and sound operating practices, surface and groundwater pollution Comparison of available ash pond and SO2 scrubcan be avoided. ber liquors indicates that the dissolved solids and trace metals concentrations in both types of liquors fluctuate greatly depending on pH, fuel composition, SO, reactant composition and concentration, and operating conditions. Since many of the sludge samples examined thus far have contained varying amounts of ash, it is possible that pollution potential would have existed from ash ponds even if no SO₂ control were employed. Ash is typically disposed of by ponding by the utility industry. The construction, lining, and operation of ash ponds are established technologies. Additional technology required for scrubber sludge disposal includes dewatering and stabilization

processes. Although these have been developed, the economics are uncertain at this point. Further technical refinements may be necessary once additional full-scale data become available. The results of numerous studies now underway at pilot plants and full-scale systems around the country will soon provide additional information in this area, as well as providing improved data on the chemical and physical properties of untreated and treated (fixed) sludge and its permeability and leachability. It should be noted that if necessary sludge can be stabilized now, but in most cases final disposal can wait until more experience has been gained.

The following report contains a discussion of technology available for the disposal, treatment, and handling of lime/lime-stone sludges. Necessary chemical and physical data describing the waste material are presented. The potential water pollution and land reclamation problems are quantified to the extent possible with available data. In conclusion, based on presently available data, there are no insurmountable technological problems in disposing of sludge in an environmentally acceptable manner.

1.0 <u>INTRODUCTION</u>

One of the major problems inherent in any flue gas desulfurization system is the necessity to dispose of or utilize large quantities of sulfur removed from the flue gas. The sulfur compounds produced by flue gas desulfurization systems fall into two general categories: throwaway or saleable products. Lime/limestone scrubbing systems generate a throwaway sludge with little commercial value at the present time. Lime scrubbing processes ordinarily produce sludges containing $CaSO_3 \cdot \frac{1}{2}H_2O$, $Ca(OH)_2$, $CaSO_4 \cdot 2H_2O$ and $CaCO_3$; limestone sludges generally contain $CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$, and $CaCO_3$. For coal-fired installations where efficient particulate removal is not installed upstream of the wet lime/limestone absorber, such sludges can contain large quantities of coal ash.

The amount of sludge generated by a given plant is a function of the sulfur and ash content of the coal, the coal usage, the on-stream hours per year (load factor), the mole ratio of additive to SO_2 , the SO_2 removal efficiency of the scrubbing system, the ratio of sulfite to sulfate in the sludge, and the percent moisture in the sludge. Table 1 lists values of these various sludge parameters for a typical Ohio plant and a hypothetical plant representing the National average expected between 1973 and 1980.

The sulfur and ash content of coal will vary from plant to plant. According to FPC data the average coal burned in Ohio in 1971 contained 3.33% sulfur and 12% ash.

TABLE 1

TYPICAL SLUDGE PRODUCTION PARAMETERS

Sludge Production Parameters	Typical Ohio Plant	National Average*
Coal:		
Sulfur Content	3.33%	3.0%
Ash Content	12%	12%
Plant:		
Load Factor	65-80%	73%
Coal Usage	.4 kg/kw-hr	.4 kg/kw-hr
Scrubbing System:		
SO _s Removal Efficiency	80-90%	85%
Moisture in Sludge	20-60%	50%
CaO/SO _s (inlet) Mole Ratio	1.0	1.0
CaCO ₃ /SO ₂ (inlet) Mole Ratio	1.2	1.2
Sulfite/Sulfate Mole Ratio	9:1	9:1

^{*} The values listed as the National average represent a mix of Western and Eastern plants expected in 1980 based on the trends shown by present flue gas desulfurization system orders.

The SO_2 removal efficiency will vary from one flue gas desulfurization system to the next as a function of local requirements. Air pollution control regulations adopted by the State of Ohio call for reduction of SO_2 emissions in certain high priority areas of the state to 1.8 mg/Kcal (1 lb/ 10^6 BTU) by July 1, 1975. An SO_2 removal efficiency of about 85% will be required to meet the standard for plants burning 3.33% sulfur coal.

Since unreacted additive is disposed of with the sludge, the stoichiometry of lime or limestone addition, that is, the CaO/SO_2 or $CaCO_3/SO_2$ mole ratios, greatly influences the amount of sludge to be handled. The CaO/SO_2 and $CaCO_3/SO_2$ mole ratios vary from system to system at present but the general trend is toward lower values as operating experience is gained. It is expected that reasonable values for this ratio will be 1.0 and 1.2, respectively.

Other factors influencing the amount of sludge to be handled are the load factor of the plant, the coal use rate, and the mole ratio of sulfite to sulfate in the sludge. The amount of sludge produced by a plant is directly proportional to the number of hours per year that the plant operates and the coal usage of the plant. The 6400 hr/year and .4 kg/kw-hr (0.88 lb coal/kw-hr) values used for those calculations are typical of large modern generating stations (DU-044, SU-031). Obviously if the plant is on line a larger fraction of the year or more coal is required per kw-hr, the amount of sludge produced will increase. The sulfite to sulfate ratio in the sludge affects the weight of the sludge produced as $CaSO_4 \cdot 2H_2O$ is heavier than $CaSO_3 \cdot \frac{1}{2}H_2O$. The ratio assumed in this paper (9:1) is taken from the SOCTAP report (SU-031). However, some

system designers are considering trying to completely oxidize the sludge to improve settling characteristics and decrease chemical oxygen demand. If this were done on a widespread basis the weight of dry sludge produced per plant would increase but improved settling characteristics would tend to lower the proportion of water in the sludge. This would enhance solid/liquid separation of the waste and possibly reduce land reclamation problems associated with sludge disposal.

Table 2 shows the quantities of ash and sludge produced per year by a 1000 MW coal-fired Ohio generating station controlled by lime/limestone flue gas desulfurization systems. The National average sludge and ash production statistics are shown for comparison.

Using the forecast demand for flue gas desulfurization given in the SOCTAP report (SU-031) and the National average annual sludge production rates per 1000 MW of controlled generating capacity, the amount of wet ash containing sludge (50% moisture) that will have to be disposed of annually by 1980 is predicted to be 113 million metric tons (125 million tons). This value is based on the assumption that there will be 116,000 MW of generating capacity controlled by 1980 and that 75% of the control will be by lime/limestone scrubbing systems.

In a related report it was predicted that 70% (12,400 MW) of the existing 1971 Ohio generating capacity could be retrofitted (RA-089). Assuming a growth rate of 7% in installed generating capacity the total Ohio generating capacity that would need to be controlled would be 16,400 MW by 1975 and 21,250 MW by 1978. Using these estimates, the amount of wet ash containing sludge (50% moisture) that would be produced annually in Ohio would be 30 million metric tons (33 million tons) by 1978.

TABLE 2

TYPICAL QUANTITIES OF ASH AND SLUDGE PRODUCED PER YEAR BY A 1000 MW COAL-FIRED GENERATING

STATION CONTROLLED WITH LIME/LIMESTONE FLUE GAS DESULFURIZATION SYSTEMS

	Ohio	National Average
Coal Ash, dry	307,000 metric tons/year	307,000 metric tons/year
Coal Ash, wet (80% solids)	384,000 metric tons/year	384,000 metric tons/year
Limestone Sludge, dry*		
CaSO₃ · ½H₂O	234,000 metric tons/year	264,000 metric tons/year
CaSO ₄ ·2H ₉ O	27,000	39,000
CaCO ₃ Unreacted	84,000	99,000
TOTAL	345,000 metric tons/year	402,000 metric tons/year
Limestone Sludge, wet (50% solids)	690,000 metric tons/year	804,000 metric tons/year
Limestone Sludge, wet (with ash)	1,304,000 metric tons/year	1,418,000 metric tons/year
Lime Sludge, dry*		
Ca SO₃ ·½H₃ O	234,000 metric tons/year	264,000 metric tons/year
CaSO ₄ ·2H ₉ O	. 27,000	39,000
CaO Unreacted	20,000	43,000
TOTAL	281,000 metric tons/year	346,000 metric tons/year
Lime Sludge, wet (50% solids)	562,000 metric tons/year	692,000 metric tons/year
Lime Sludge, wet (with ash)	1,176,000 metric tons/year	1,306,000 metric tons/year
ASSUMPTIONS:		
Coal:	3.33% S; 12% Ash	3.0% S; 12% Ash
Plant:	6400 hr/yr; .4 Kg Coal/kw-hr	6400 hr/yr; .4 Kg Coal/kw-hr
Scrubber:	85% SO _g Removal 1.0 CaO/SO _g (inlet) Mole Ratio 1.2 CaCO ₃ /SO _g (inlet) Mole Ratio	85% SO ₉ Removal 1.0 CaO/SO ₉ (inlet) Mole Ratio 1.2 CaCO ₃ /SO ₂ (inlet) Mole Ratio

^{*} Sulfite/sulfate ratio based on performance of Chemico scrubbing unit at Mitsui Aluminum Co., Japan.

The solid waste disposal problem presented by lime/limestone scrubber sludges can be put in perspective by comparison to other industries and activities. presents the quantities of waste, typical compositions, disposal methods, and potential environmental problems for some of the major solid waste producing activities in Ohio and other states. It can be seen that in terms of quantity, estimated Ohio scrubber sludge production in 1978 will present a disposal problem similar to that provided by the present disposal of municipal refuse in Ohio. Because of its lower density, however, the volume required for refuse disposal is eight to ten times greater than would be required for scrubber sludge. In terms of weight the present disposal of phosphate rock slime and gypsum from fertilizer manufacturers in Florida alone presents a problem two to three times that of scrubber sludge in Ohio. mation presented in this table shows that solid waste from other industries presents problems of greater magnitude and of no less serious natures than that posed by scrubber sludge.

Ponding and landfilling provide the major mechanisms of disposal for most solid waste products. In terms of land use and reclamation, these disposal mechanisms have many points of similarity for various industries. Land use for waste disposal may be esthetically objectionable. The wastes could provide varying degrees of surface and groundwater pollution depending on chemical composition, solubilities, and the location, design and operation of the disposal site. For land reclamation, most of the stable wastes will require only a cover material to support vegetation and prevent eventual erosion. However, some wastes are very resistant to dewatering and could reslurry in the pond or landfill. If this is shown to be true, it is likely that fixation will become a necessary practice.

TABLE 3 COMPARISON OF MAJOR SOLID WASTE DISPOSAL PROBLEMS

Waste Material	Quantity Disposed of Annually (dry basis)	Composition	Method of Disposal	Land Use or Reclamation Problems	Environmental Considerations
Phosphate Rock Slime from Fertilizer Manu- facturer ¹	36,000,000 (1967)	4-6% Solids Solids Composition: P ₂ O ₆ 9-17% Al ₂ O ₃ 6-9% SiO ₂ 31-46% CaO 14-23% Fe ₂ O ₃ 3-7% MgO 1-2% F 0-1% Trace Elements	Ponding	Possible Bogs (Settles to only 30% solids after years. Not established wheth- er dried solids will support vegetative growth.)	1 Iosebata to
Gypsum from Fertili- zer Manufacturer ³	25,000,000 (1973)	85-90% Solids Solids Composition: CaSO ₄ ·2H ₈ O 100%	Ponding and Sur- face Piles	Cover material required for plant growth.	Potential ground and surface water pollution.
Ohio Municipal Refuse [®]	18,000,000 (1973) ⁶	Garbage, Paper, Wood, Metals, etc.	Landfill and Incineration	Cover material needed to support vegetation.	Potential ground and surface water pollution; potential air pollution.
Ply Ash from Ohio Power Plants	10,000,000 (1978)	80% Solids Solids Composition: SiO ₂ 30-50% MgO 1-10% Al ₂ O ₃ 10-20% K ₂ O 1-5% Fe ₂ O ₃ 10-25% C 1-3% CaO 2-20% Trace Elements TiO ₂ 0.2-2%	Ponding and Land- fill	Needs cover material.	Potential ground and surface water pollution
Scrubber Sludge from Ohio Power Plants ^a	17,000,000 (1978) ⁶	50% Solids Solids Composition: CaSO ₃ ·½H ₂ O 36% CaSO ₄ ·2H ₂ O 4% CaCO ₃ 12% Fly Ash 48% Trace Elements	Ponding and Land- fill	Possible Bogs (difficult to de- water if untreated); needs cover ma- terial.	Potential ground and surface water pollution.

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^{80%} disposed of in Florida.

^{3.} Personal Communication, Mr. Stowalzer, Bureau of Mines, Phosphate Commodity Office, August, 1973. 4. 80% disposed of in Florida.

Personal Communication, Norbert Schomaker, OSWNP-EPA, August, 1973.
 Excludes agricultural and mining wastes.

^{7. 24,550} MW of installed coal-fired generating capacity in 1978; 73% load factor; 0.4 Kg Coal/kw-hr; 12% ash.

^{8.} Without ash.

^{9.} Assuming that 21,250 MW out of an anticipated total coal-fired installed generating capacity of 24,550 MW is controlled by limestone scrubbing systems; 73% load factor; 0.4 Kg Coal/kw-hr; 3% sulfur; 85% SO₂ removal; 1.2 CaCO₃/SO₂ (inlet) mole ratio; 10% oxidation.

2.0 <u>NATURE OF THE MATERIAL</u>

The environmental effects of sludge disposal will be dictated by the chemical and physical properties of the material, and these properties may vary widely for different operations. Important variables include the sulfur and ash content of the coal, the type of scrubber operation (lime or limestone) and amount of excess material added, the amount of ash in the sludge, the type of limestone (limestone or dolomite), type of recycle (closed loop, open loop, or partially closed loop), the degree of dewatering of the sludge, and the degree of oxidation of the sulfite. Several studies are currently underway to quantify the influence of these variables. Those data which are available are presented in this section. It should be noted that only recently has a signigicant effort been extended to characterize sludge materials. The information presented in this section should be considered preliminary until additional test data are available. EPA's program with Aerospace Corporation (Contract 68-02-1010) should be particularly important in providing further understanding of these materials.

One potential environmental effect of considerable concern is water pollution, both surface water and groundwater; and it is the chemical properties of the sludge which are relevant to this area. Another environmental concern is land reclamation of disposal sites, and it is the physical properties of the sludge which are most relevant to this area. Chemical and physical characteristics of the sludge will be discussed separately.

2.1 Chemical Properties of Sludge and Related Materials

The potential water pollution problems derived from the chemical properties of the sludge can be broken down into

the following categories:

- 1. Soluble toxic species (toxic meaning elements which can cause health problems even at low concentrations),
- 2. Chemical oxygen demand,
- 3. Excessive total dissolved solids,
- Excessive levels of specific species,
 e.g., sulfate and chloride, not
 generally thought of as toxic,
- 5. Excessive suspended solids (some of which might dissolve later).

Some data have already been generated which help to put these potential problems in perspective. It should be noted, however, that the great majority of these data have been generated in laboratory studies, pilot plants, or large units which do not have a lengthy record of continuous operation. It is, therefore, not clear how closely the results parallel those that would be obtained by a large system in continuous operation. In addition, since almost every system is unique in terms of the coal, limestone, and scrubber system parameters, the results should best be interpreted as trends rather than as established facts.

Data describing the chemical compositions of coal and coal ash are given in Tables Al and A2 (all tables prefaced by the letter A are in Appendix A). These analyses are important for several reasons. First, in many cases the ash will be disposed of together with the sludge. Therefore, ash composition will affect composition of liquors associated with potential leachate

and runoff. Secondly, ash ponds alone may possibly be no less potentially harmful than sludge ponds with respect to the total dissolved solids as well as heavy metal concentrations. The fuel is one of the chief origins, along with the lime or limestone and even makeup water, of these species. Data sets 1 and 2 in Table Al compare the trace element compositions found in an Eastern versus a Western composite coal sample. Relative to the Western coal, the Eastern coal is very high in boron, lead, zinc, manganese, barium, chromium, and vanadium. The Western coal, on the other hand, contains greater amounts of arsenic, antimony, selenium, and nickel. The chlorine content may prove to be of special concern because of its effect on trace metal solubility. The chloride ion, which is extremely soluble and is capable of forming soluble metal complexes with a number of elements, could promote solution of toxic metals in pond liquors.

Analyses of fuel ashes, including Western and Eastern coal bottom ashes and several fly ash samples, are also given in Table Al. Although it is not possible to trace an element's ultimate disposition to bottom or fly ash because of the inconsistency of available data, some trends may be noted. Examination of data sets 3 and 7 reveals that except for manganese and cadmium, fly ash contains considerably greater concentrations of all trace elements measured for that Western coal. Sets 5 and 6 illustrate that all elements measured except bromine, chromium, and yttrium became more concentrated in the fly ash by passage through TVA's turbulent contact absorber (TCA) scrubber at Shawnee.

Typical concentration ranges for major and minor constituents of U. S. fly ashes are included in Table A2. Also shown are comparative values for fly ash from a lignite versus a bituminous coal. These data serve to indicate the wide variation found in typical fly ashes.

The purpose of Table A3 is two-fold. The data show the variation in composition of particulate in a fly ash pond with respect to location of sampling point. This variation corresponds to the change with respect to retention time in the pond. These particles which do not settle out are represented by Samples B and C which are buoyant fly ash microspheres. In this sample set, aluminum, barium, lead, and iron particulate concentrations tended to decrease as the particles travel through the pond. In many instances, however, the concentrations in the solid phase either remain constant or increase. Liquid phase analyses of fly ash ponds are limited. The pH values reported range from slightly acidic to alkaline. Some ash liquors, however, are known to be so highly acidic that neutralization prior to ponding is necessary (private communication).

Another possible origin of pollutants in air pollution control system sludge besides the fuel is the lime or limestone employed as the SO_2 reactant. Table A4 presents available analyses of several limestones.

Table A5 gives some analyses of major and minor species found in sludge samples collected from eight units around the country. This table demonstrates the variability which may occur between different sludge samples. The trace elements present in the sludge may originate from either the coal, the lime or limestone (or other SO₃ reactant), or the makeup water. Table A6 gives the content of metals and other trace species for the solids collected at various points in a TCA limestone scrubber.

Their final distribution in the solid and liquid phases can be used to predict whether or not a water pollution problem exists, either from the pond effluent or from landfill leachate. In Table A7 it is interesting to compare the relative amounts of

metals in the clarifier solids with those in the liquid associated with the solids from a prototype limestone TCA scrubber operating in partially closed loop. As might be expected, sodium, potassium, magnesium, and calcium are soluble. However, such species as boron, molybdenum, manganese, silicon, and copper also occur at significantly higher levels in the liquid. Other trace metal species are concentrated in the solids. It should be noted that equilibrium may or may not have been reached, i.e., given time additional solids might dissolve.

The concentrations of various species in the solid and liquid effluents from a centrifuge can be compared in Table A8. These data are from a limestone turbulent contact absorber (TCA) scrubber pilot plant; the fuel was a Western coal. It can be seen that many metals are concentrated in the liquid phase, including iron, aluminum, magnesium, sodium, boron, titanium, manganese, chromium, copper, and nickel. The pH of this liquid is not known, but a low pH might account for the high metal solubility. In Table A9 the relative content of metals in the scrubber output solids versus the centrifuged solids can be compared for this same pilot plant. These data were obtained employing a different analytical technique.

A few chemical analyses of scrubber liquors at various points throughout the system are available. Table AlO gives interesting results for a pilot plant scrubber which uses fly ash as the absorbent material. Analyses for dissolved species are presented, and compared to Public Health Service Standards. The low pH (3.3) of the scrubber recycle liquor is noteworthy, and probably accounts for the relatively high levels of some metals. The lime treatment of the recycle water raises the pH to 9, and considerably reduces the solubility of the metals; however, boron, cadmium, lead, and manganese are still present at levels high enough to be of some concern.

Scrubber liquor compositions are expected to vary under open versus closed loop operation. Several sets of data are available to illustrate this. Tables All and Al2 present concentrations of major species in clarifier effluent samples from TVA pilot plant limestone systems. The open loop concentrations are surprisingly high, especially chloride and total dissolved solids. Table Al3 compares some metal concentrations for open and closed loop operation of a pilot plant to Alabama effluent guidelines. Zinc, nickel, iron, copper, and cadmium are higher for open loop operation than for closed loop. pH values are not given. All metal effluents are below the guidelines.

Information presented in Tables Al-Al3 indicates that careless disposal of untreated scrubber sludge may pose some environmental problems in terms of surface or groundwater contamination. The data on chemical compositions of scrubber liquors are of particular significance in this regard. Using standards for permissible limits in drinking water as a reference, some scrubber liquors have excessive amounts of one or more of the following: manganese, lead, copper, cadmium, selenium, boron, nickel, magnesium, chloride, sulfate, and total dissolved solids. In many cases the drinking water standards are not greatly exceeded but sulfate and total dissolved solids are generally far in excess of the limits. In regard to the metals it appears that pH is an important factor, a high pH reducing the metal content. Limestone sludge liquors typically have a pH in the range of 5 to 7, while lime system liquors are more alkaline, possibly having a pH as high as 10. These numbers can vary widely, however, depending to a large extent on the amount of ash present. appears that sludge liquors are generally of much higher dissolved solids content than ash liquor and both liquors contain scattered levels of trace metals although the scarcity and variation of available data makes interpretation difficult. For some sludges containing large amounts of ash, radioactivity might present an occasional problem.

The fact that the sludge does contain significant quantities of soluble material indicates that considerable care will be required in the design and operation of sludge disposal projects. The particular cases of ponding and landfill disposal are treated at length in later sections.

2.2 <u>Physical Properties and Settling Characteristics</u> of Scrubber Sludges

As for the chemical properties, physical properties of sludge may vary widely, and may be influenced by many factors in a manner that is not yet well understood.

The physical properties are important in terms of initial sludge disposal since they have an influence on the difficulty of handling, transporting, and treating the material. Physical properties also are important in regard to land reclamation of abandoned disposal sites. The areas of potential concern here are:

- 1. Settling characteristics, i.e., ease of dewatering,
- 2. Rewatering of the dried, aged material,
- 3. Strength, i.e., load-bearing capability,
- 4. Ability to support vegetation growth (chemical properties also are important here).

This section presents those data that are presently available on physical properties of sludge. As for the chemical properties, it is important to note that those materials tested so far may not be typical of the material which will be obtained from a large scale continuous operation.

Particle size measurements have been reported by Dravo for a number of sludge compositions (SE-066). Both wet screen and sub-sieve analytical techniques were utilized. The results are presented in Tables Al4 and Al5. Identification of the samples analyzed is given in Table Al6.

A related parameter, Blaine Index, which is a measure of total surface area of dry solids, was also determined. ASTM method C204-55, which measures the permeability of a packed bed of material, was used in this study. Since two entities, permeability and Blaine Index, are inversely related relative degrees of permeability may be ascertained from the results presented in Table A17 (SE-066).

The bulk density of various scrubber sludges varies similarly as a function of water content. As the percent of water increases from zero, the bulk density increases as the pore volume becomes filled. When completely filled, a maximum bulk density is reached. With greater percentages of water, a dilution effect is observed as the bulk density decreases. For Shawnee clarifier underflow samples from a limestone scrubbing system with simultaneous fly ash removal, the peak bulk density was reported to be 1.7 g/cm³ at 30% water content. The bulk density of a packed and dried Shawnee sample was 1.20 g/cm³. These data are compared to the true density of Shawnee solids equal to 2.48 g/cm³ (AE-008). The peak bulk density for an individual sludge will depend on the nature of the scrubber system from which it was obtained. For example, the sludge from a western power plant employing a limestone system was shown to have a maximum bulk density of 1.87 g/cm³ at 22% water content.

Viscosity measurements for Shawnee limestone scrubber sludges and sludge from a western coal-burning plant with limestone scrubbing have also been reported (AE-007, AE-008, AE-009). The Shawnee samples, 50-60% solids, exhibited a viscosity which decreased with stirring time. The other sludge tested displayed markedly different properties. In fact, the sludge settled so rapidly and was so viscous that measurements were limited to those less than 50 poise. Some of the especially stiff mixtures displayed sporadic rheopectic behavior, i.e., the viscosity increased with stirring time. This behavior is the opposite of that observed with Shawnee sludges.

Based on preliminary results of experiments designed to study settling properties of scrubber wastes produced by lime/ limestone systems, this phenomenon is not expected to result in extensive separations. From a bench-scale experiment conducted by TVA, a settling rate of 5 cm/hour was observed for the first and second phases of settling, which were defined as the induction period during which floc formation occurs and the second stage, free settling (SL-034). The third phase is compression settling, i.e., when the flocs begin to touch each other and gel formation occurs. The settling rate during this stage was greatly reduced. After 48 hours the settling rate decreased to practically zero and no further settling was observed, even over a period of several months.

It has been reported that limestone sludges with high sulfate content settle to 45% solids with no drainage provided. This is compared to final settled solids content of 50% with underdrainage. Sludges having high sulfite content settle only to 35% solids regardless of whether drainage is provided (RO-084). Dravo Corporation compared solid contents of various power plant wastes after one day of settling. The data are presented in Table A18 (SE-066).

Settling characteristics of lime/limestone scrubbing sludges are directly related to the degree of compaction. The factors affecting this parameter include the following, all of which are currently under investigation by TVA (SL-034).

- · Hydraulic head
- Ash content
- Degree of oxidation
- · Stirring
- Agglomeration
- · Lime vs. limestone

Results of bench-scale studies indicate that increasing the height of the slurry column increases the degree of compaction. When the height of an experimental column was increased from 13 cm to 100 cm, compaction was increased by 15%. It is predicted that a high ash content in the sludge would also produce favorable effect on settling although no data are available to support this point.

Degree of oxidation is under intensive study. It is known that calcium sulfate crystals, because of their large blocky nature, settle better than the thin plate-like calcium sulfite hemihydrate crystals. Thus, oxidation to sulfate should improve the degree of compaction. It has been reported that a high degree of oxidation is required, however, to produce a noticeable effect. Methods under study to promote oxidation of limestone scrubber slurries include:

- · Air introduction into the scrubber,
- · Oxidation in separate unit,

- · Spinning cup oxidizer,
- · Use of catalysts.

Identification of scrubber conditions which promote agglomeration of sulfite crystals has not been made yet. Some sulfite crystal agglomeration has been noted. Flocculating agents are being investigated to determine their effectiveness in promoting appreciable agglomeration.

The data presented above describes the physical properties of scrubber sludge from various pilot operations. It should be pointed out that there are several large-scale projects underway or planned that should supply data on the long-term physical properties of sludge. These projects are discussed in Section 4.0.

3.0 <u>DISPOSAL OF SCRUBBER SLUDGE</u>

Several methods are being considered for disposal of waste material generated by lime/limestone scrubbers. The most common approaches are ponding of untreated sludge and landfilling of treated and untreated material. Other possibilities which have not received much attention thus far are deep well injection and mine subsidence.

The first two mentioned are the chief methods used by the utility industry to dispose of ash from fuel combustion. Most technology available to date is based on experiences with that material. Technology associated specifically with sludge is just now under development, thus posing a shortage of available information in that respect. The following sections describe the various features of each disposal operation and, on the basis of available data, present the potential impact on water pollution. Land reclamation aspects for both ponding and landfill are dealt with in a single discussion because of the similarity of an abandoned, dried-up pond and an exhausted landfill.

A major factor in the selection of a disposal method is the geology of the proposed site. There are several basic types of geologic features in the State of Ohio. It is difficult to generalize, however, due to the great extent of variation within each type. Basically, approximately two-thirds of the state is covered with glacial deposits. These glaciated areas fall into two general categories, the glacial tills and glacial moraines. The tills are characterized by soil of high clay content, thus resulting in a region highly impermeable to water flow. The moraines, on the other hand, are generally permeable because of the large sand, rock, and gravel composition. The eastern and southeastern sections are non-glaciated areas having

distinctly different features. This region is densely populated with mining sites. The bedrock remains exposed since no glacier movements were experienced here. The permeability associated with this region is dependent on the type of bedrock in each location. Limestone bedrock is selectively permeable; sandstone is generally permeable; and shale bedrock is relatively impermeable.

The river valleys located throughout the state are the regions of greatest concern for surface waste disposal. These are composed of alluvial fill, which is a very coarse combination of sand, gravel, and rocks. The high degree of resulting permeability makes Ohio's river system, in general, a prolific aquifer experiencing continuous recharge along the watercourse.

Thus, the State of Ohio contains a wide range of geologic and hydrogeologic features. This necessitates an investigation of each proposed disposal site prior to its design to ensure a minimum of environmental hazard potentially posed by sludge leachate.

An alternative to disposing of the scrubber sludge is commercial utilization. Development in this area is currently in progress under both government sponsorship and private industry.

3.1 <u>Methods of Disposal</u>

In this section of the report the technical and potential pollution aspects of ponding, landfill, and other less promising disposal schemes are described.

3.1.1 <u>Disposal by Ponding</u>

Disposal of wastes by ponding has historically been a favored technique in a number of industries, e.g., gypsum sludge from fertilizer plants, phosphate slime from phosphate mining, and fly ash from coal burning facilities. The mechanics of pond construction and pond operation are well known; however, much of this technology was developed with less regard for environmental effects than is now required. This is particularly true in regard to (1) loss of pond liquor by percolation into underlying aquifers, and (2) allowing overflow into surface In the past, there was often little attention paid to pond site selection or to pond lining. The general attitude seemed to be that fine particles from the pond liquor would eventually plug the soil and minimize percolation. Nowadays, careful study of pond sites will be necessary and when there is a danger of groundwater pollution suitable pond linings must be provided. Changes in regard to pond overflow may be especially significant. In the past dilution by the receiving stream was considered to provide acceptable treatment. Regulations are moving toward a "no degradation" basis which means pond overflow must be eliminated in almost all cases. This will require total recycle of pond liquor.

One attraction of ponds is that the volume can be increased as needed by building up the sides of the pond. In some cases (e.g., gypsum sludges from the fertilizer industry) the pond walls can be built up using settled solids from within the pond. In the case of scrubber sludges this may require special treatment of the sludge. Ponded scrubber wastes are typically not stabilized; however, stabilization of that sludge used for building up the walls via certain commercial processes (to be discussed later) might provide a suitable approach.

3.1.1.1 Pond Management

The start-up and day-to-day operation of a disposal pond involves answers to the following questions pointed out by Slack and Potts (SL-034).

- Will the pond be operated as a single unit or divided into sections?
- Will the original depth be the limit or can walls be built up using the settled material?
- · Will the pond be partially filled with water before operation begins?
- Can the pond be filled to the top of the dike or must some freeboard be allowed?

The first question is related to the settling characteristics of the material as previously discussed (Section 2.2). Ash ponds are typically operated such that the slurry enters one end of the single pond. As it flows to the opposite side, the well-settling ash drops out and a pool of supernatant forms at the far end. The effluent is removed via weirs or standpipes, thus allowing continuous operation of the pond until full. In contrast, waste gypsum from phosphoric acid manufacture is usually ponded in several units. Since the settling characteristics of the waste are poor, one pond is allowed to dry and be emptied while another pond is being filled.

The second question deals with the dimensional stability of the settled material. In ash pond management, the settled ash is seldom used to extend the height of the walls because its spherical form results in a low angle of repose. Waste
gypsum, on the other hand, lends itself readily to this application. Excavating equipment is employed to pile up the dried
material as high as 30 meters. Preliminary data for untreated
scrubber sludges presented in Section 2.2 are not yet sufficient
to predict whether this type of operation could be successfully
applied.

If the scrubber is operated under closed-loop, smooth start-up may necessitate partial filling of the disposal pond before hand. This would provide a source of recycle water at the onset of operation and eliminate the need for additional start-up pumping arrangements. This would produce overall increasing concentrations with respect to composition of liquor associated with solids until steady state is achieved.

The amount of freeboard required for any particular pond is chiefly a function of climate. If the area receives large amounts of precipitation during periods when evaporation rate is low, then more freeboard would be necessary than for ponding operations in hot, dry climates. Ponds which lack drainage provisions would also tend to require greater free-board.

3.1.1.2 Water Pollution Potential and Control for Ponding

Potential hazards associated with contamination of surface and/or groundwaters by sulfur oxide sludges exist in the following areas:

- soluble toxic species (toxic meaning elements which can cause health problems even at very low concentrations),
- · chemical oxygen demand due to sulfite,
- · excessive total dissolved solids,
- excessive levels of specific species, e.g., sulfate and chloride, not generally thought of as toxic,
- · excessive suspended solids.

These could promote problems via leachate and/or runoff routes. Although similar in nature, these routes will be considered separately in this presentation.

Leachate from Sludge Disposal Ponds

The composition of the leachate formed is a function of several factors including chemical composition of the sludge, pH, solubility of the individual species present, and age of the disposal site. The nature of the leachate expected from untreated sludge can be judged by analysis of liquors associated with scrubber samples, especially clarifier supernatant or scrubber recycle water in closed-loop operation. Since fly ash will be collected and/or disposed of together with the scrubber sludge in many cases, it is likely that many of the potentially leachable elements originate with the ash. Although ash ponds have been in operation for years, there has been little concern with environmental contamination either by high dissolved solids

content or by trace element constituents of the pond waters. Both have recently been shown to be present in varying amounts in several ash pond samples.

A disposal pond provides maximum opportunity for contamination of groundwater. Unlike a landfill, the sludge is always saturated with water, and the "head" of liquor in the pond assures a continuous driving force for percolation. Underlying strata will also become saturated, and if an unconfined aquifer exists beneath the pond, the pond site will act as a "recharge" zone for that aquifer. If no unconfined aquifer exists, the pond liquor will continue to seep into the existing strata beneath the pond. It is not clear whether this would be construed as a detrimental environmental impact.

Given that an aquifer does exist, the important factors are the rate at which pond liquor permeates into the groundwater and the chemical composition of that liquor as it enters the aquifer (any suspended material will probably be filtered out by the soil).

It should be noted that vertical and especially lateral movement of groundwater can be very slow, e.g., about a meter per year. It also is important to note that groundwater movement may occur in a "plug flow" fashion. Given that a pollution source exists above an aquifer, vertical flow of polluted water into the aquifer may be greater than the natural lateral movement of the groundwater. This, plus the "plug flow" nature of groundwater means that there may be little opportunity for dilution of the polluted water even over a period of years. This situation is very different from the case of allowing pond overflow to enter a stream, where even high pond liquor concentrations may be diluted in a matter of minutes. It can be seen that it might be many years

before a groundwater contamination problem would be discovered by some groundwater user down-gradient from the site. It should also be noted that unless carefully designed even a disposal pond monitoring program might take years to produce useful results.

With regard to groundwater contamination by constituents of pond liquor, there are some possible mechanisms to reduce the impact of the pond liquor. These involve a group of reactions commonly referred to as "soil attenuation" mech-Reactions between solution species and soil particles can occur via adsorption, ion exchange, or precipitation. ion exchange and precipitation are essentially displacement of one ion by another, only simple adsorption provides a true removal mechanism. For ion exchange and precipitation, it is to be hoped that a toxic species might be lost from solution and a less toxic species gained, however, there is no assurance of It is unlikely that a large change in total dissolved solids would occur via soil attenuation mechanisms. solved species might, however, move through the soil slower than the liquid in which they entered. Unfortunately, no data are yet available on this important topic for scrubber sludge liquors although the soil type is clearly important. A large study of soil attenuation mechanisms is being done for municipal wastes under the sponsorship of the Office of Solid Waste. experimental program is just getting underway, however, and no results are yet available.

STEAG, a government organization in West Germany, has instrumented a sludge disposal pond for lime scrubber sludge to determine effects on groundwater. This group has been visited and a description of their system obtained. Their system is described in detail in Appendix B. So far their monitoring

system has not detected any contamination of the aquifer which is located only about a meter below their unlined pond. However, their observation wells are far enough away from the pond that sufficient time probably has not elapsed for any contamination to reach the wells. Combustion Engineering and Kansas Power and Light are also doing a study of this type, but no results have been released.

There is one piece of information which, although not well documented, seems to be of significance in regard to pollution of groundwater by leachate. That is that no pollution problems have been documented due to ash pond leachate, even though ash ponds have been widely used for decades, mostly without liners, and in all types of soils. It seems reasonable that if pollution problems resulted from this practice they would have been discovered by now, especially if toxic species were involved. High total dissolved solids, sulfates, and chlorides might be passed unnoticed since they occur naturally in many aquifers. However, toxic species should have been The effect of pH on trace metal solubility is great; therefore liquors having a relatively low pH, such as ash ponds for high sulfur coal or limestone sludge ponds, may pose a greater threat in this respect than liquors associated with lime scrubbing systems or alkaline ash, for example. Nevertheless, the fact that no problems have been traced to ash ponds is encouraging.

Even though no problems have been attributed to ash ponds the information on the chemical properties of sludge indicates a need for proper site selection and possibly lining of ponds. In some situations a continuing monitoring program may be necessary, for example, when a disposal pond is to be located over an unconfined aquifer.

Overflow of Pond Liquor

Disposal ponds have typically been operated with less than total recycle of pond liquor. The excess liquid has often been permitted to flow into receiving streams with little treatment beyond neutralization, settling, or skimming. Accidental spills have occurred frequently.

Newer and more stringent regulations on waste water disposal will likely reduce the practice of overflowing excess liquor into lakes and streams. This will necessitate the use of closed loop (total recycle) operation for scrubber sludge disposal by ponding, with treatment of any blowdown streams. Alternatively, blowdown streams might be disposed of via evaporation or disposal in the ocean. This sort of operation, combined with proper site selection, design, and lining of ponds could eliminate contamination of surface or groundwater by ponded scrubber sludge, thus making ponding a viable method for sludge disposal. A problem which might remain, however, would be the eventual land reclamation of the pond site due to the resistance to dewatering exhibited by many unstabilized sludges.

Control of Pollution Potential from Ponding

Pond linings have been finding greater favor in recent years. In some cases the intent has been to decrease pollution, in other cases the intent has been to avoid loss of water which could be recycled. In many areas, clay, concrete, wood, or metal has been used as a liner. Recently synthetic linings are finding increasing usage. These include the following materials (KU-061):

- · Polyvinyl Chloride
- · Natural Rubber
- · Synthetic Rubbers
- · Polyethylene
- Polypropylene
- · Nylons

With so many varieties of membranes on the market, it is sometimes difficult to select the material suitable for the desired purpose. The following criteria may be helpful.

- The liner should have high tensile strength and flexibility and should be able to elongate sufficiently without failure. It should resist abrasion, puncture, and the fluid to be stored and should conform to other desired physical properties.
- Should have good weatherability and a guaranteed long life.
- · Should be immune to bacterial and fungus attack.
- It should be able to stand the desired temperature variations and other ambient conditions.

 It should be capable of being repaired easily at any time during its life.

A leak detection system may be built into the pond system. Two types of leak detection systems are:

- (1) Underbed Drainage System. This consists of a network of gravel packed drainage canals or perforated drainage pipes. All seepage is channeled to the outer perimeter of the pond and collected in a sump outside the pond, where inspections can be made. variation is to monitor the fluid in standpipes (piezometers) placed within the pond. The tops of the pipes extend above surface level; the bottoms penetrate the liner into the underlying soil. Wells in the proximity of the ponds may also be utilized.
- (2) Ground-Resistivity Measurement System.
 Several metallic pins may be buried
 beneath the pond. Using a resistivity
 meter, ground resistivity between these
 pins may be measured. A marked decrease
 in ground resistivity may indicate pond
 leakage.

Some approximate cost figures have been estimated for lined ponds (RO-084). Factors influencing the price include size and type of lining required. For a 0.02-0.04 square kilometer (5-10 acre) pond with no provision for drainage, \$1,200,000

to \$5,000,000 per square kilometer (\$5,000-20,000/acre) is estimated for clay or stabilized pozzolan base lining. The cost of a drained pond fitted with a soil covered plastic liner can be as much as \$6,200,000 to \$7,500,000 per square kilometer (\$25,000-30,000/acre).

3.1.2 Disposal by Landfill

A second approach to the problem of disposal of waste solids generated by lime or limestone scrubbing systems is landfill. Currently less than 40% of existing or planned installations have adopted this alternative, while approximately 60% have included ponding facilities. Eventually, however, ponding sites may have to be reclaimed. This possibility would necessitate future conversion to a landfill type of operation.

Characterization of lime/limestone scrubber sludge thus far has revealed a nature not readily applicable to untreated landfill disposal. The sludge does not settle or dewater readily, and the results of some experiments have indicated that once dried, the untreated material will reabsorb moisture to its original water content (see Section 3.3). This creates the unattractive possibility of the disposal site becoming a bog. A second aspect of untreated sludge is its leachate characteristics, discussed in the preceding section. For these reasons, chemical and physical fixation processes have been proposed and are now under investigation. The marketing agents for these fixation techniques claim that conversion to a physically and chemically stable landfill material is possible. In some cases, a saleable by-product can be made.

In the following discussion, the term landfill will mean the disposal of a scrubber sludge treated via dewatering and/or stabilization techniques.

The technology associated with disposal of waste scrubber sludges by landfill operations is currently in the development stage. There are three basic features requiring discussion to accurately describe the current state of knowledge regarding this disposal method: dewatering, fixation, and handling of sludge.

3.1.2.1 Dewatering Techniques

The object of any sludge dewatering process is to recover the solid content of the sludge in a concentrated form suitable for disposal or further processing. The liquid content is recovered from suspended solids for recirculation within the process or for safe discharge as a processed effluent. Presented in this section of the report is a discussion of methods available for dewatering of air pollution control system sludges. Many of these techniques have been experimentally and industrially applied to sludges generated by lime or limestone wet scrubbing systems.

Interim Ponding

An interim pond has three purposes. It is a clarification basin, a sludge dewatering area, and a sludge storage area. A single pond cannot perform all of these functions effectively. The effectiveness of ponding as a dewatering technique is a function of the settling characteristics of the

sludge. This aspect has been dealt with in a previous section of this report (2.2).

Clarification

Thickeners are currently employed in some sulfur oxide removal systems as a primary dewatering device in cases where the solids content is low. Thickeners are sized in terms of the surface area per rate of throughput; i.e., if a particular slurry settles slowly, a longer time and consequently a greater surface area is required to effectively provide separation of solids and liquor. The thickener surface area can vary from 1.0 to 10 m²/metric ton/day (10-100 ft²/ton/day) from sludge to sludge (SE-066) depending on the settling characteristics of the sludge. Limestone scrubber sludges containing unreacted additive are reported to thicken well compared to lime sludges because of the coarse limestone present, but result in a turbid supernatant. Therefore the design should be based on clarification considerations. On the other hand, zone settling rates should be the basis for design of thickeners for sludges consisting of more uniformly fine particles.

Bed Drying

The use of a porous bed for sewage sludge dewatering is common. Dewatering occurs by two mechanisms: drainage and evaporation.

In general, drainage is affected by solids content, depth of sludge application, depth of supporting media, sand grain size, degree of paving, the presence or absence of

coagulants, and the chemical composition and physical characteristics of the sludge (JE-013, JE-014). Climatic and atmospheric conditions are also important variables. These include temperature, humidity, rainfall, air velocities, barometric pressure, and solar radiation.

Aerospace Corporation is investigating the effects of underdrainage on the drainage rate employing bench-scale column studies (AE-007, AE-009). The steady state drainage rate for wet limestone scrubber sludge from Shawnee was reported to be 0.046 cm³/min. When sludge was allowed to air dry in the columns, several days were required for initiation of drainage; the drainage rate was then much less than that observed for wet sludge. Eventually, enough water was retained by the sludge column to return it to its original water content (51.7%).

The mechanism suggested for drainability of scrubber sludges involves a wicking action. If the sludge is saturated to begin with, no delay is observed for start of drainage.

The second mechanism involved in dewatering by bed drying is evaporation. In general, dewatering by evaporation occurs in two phases. Phase I is a constant drying period during which the surface moisture is exhausted until it can no longer be replenished by the interval transport of water to the sludge surface. Phase II is a falling rate drying period. This depends on the nature of the dewatering material (JE-013).

Presently, an experimental program at Hollywood, Pennsylvania, is studying the feasibility of a coal mine sludge drying basin. Three methods of drying, open sun, loose-fitting cover, close-fitting cover (solar shell effect) are being examined. Results so far are inconclusive.

Centrifugation

Centrifuges are well-suited for the separation of waste solids from a liquid suspension. This technique produces well concentrated cakes and offers a high degree of effluent clarification. Space requirements for equipment are minimal. However, they have the disadvantage of significant power consumption.

Centrifugation has been investigated by Dravo, EPA, and TVA as a possible dewatering method for sulfor oxide sludges. Results of centrifugation of various scrubber sludges have been reported by Dravo Corporation (SE-066). Most of the tests were performed with a standard laboratory centrifuge. A limited series of tests on lime scrubber sludges from Duquesne Light Company's Phillips Station was conducted using a Bird 6-inch continuous centrifuge. These results are given in Table A19.

A 75% solids content was achieved for various TVA pilot plant samples employing a centrifugal force of 1000 x gravity (SL-034). Short-term centrifuge tests conducted by EPA at Shawnee produced promising results. Limestone scrubber sludges from the clarifier bottoms were used. The results are shown in Table A20 (EL-030). Long-term tests are planned.

Because of the physical, blocky nature of sulfate crystals as opposed to sulfite, dewatering is improved by a higher sulfate/sulfite ratio. Thus, good results (85-90% solids) have been reported for a sample obtained from the Chiyoda process, which results in a sludge with an extremely high sulfate to sulfite ratio. This process is based on aqueous scrubbing of SO_2 to produce sulfurous acid followed by oxidation to sulfuric acid. Reaction with limestone at this stage produces

calcium sulfate; thus the sludge contains only negligible amounts of sulfite.

Aerospace Corporation has reported the results of a comparative study of dewatering techniques utilizing clarifier samples from Shawnee's limestone scrubber. The water content of the original clarifier sample was ~80%; centrifugation reduced the water content to 44%. Associated bulk densities were also determined, and the results are tabulated in Table A21 (AE-006). A similar study was conducted with clarifier samples from a Western power plant's limestone scrubber. These results are also shown (AE-007, AE-010). Although both clarifier samples contained approximately equal amounts of water, centrifugation resulted in greater reduction in water content with the Western plant sample. The reason suggested for this was the physical nature of the sludge; i.e., maximum density of Western sludge (1.87 g/cm^3) is achieved at a slightly lower water content (22% H_2O) than for the Shawnee sludge (1.7 g/cm³ at 30% H₂0). Further details of these physical properties were given in Section 2.2 of this report.

Vacuum Filtration

The most commonly used type of vacuum filter is the revolving drum. Some of the variables affecting the ability to dewater a sludge are:

Sludge Variables	Operating Variables
Concentration of Solids	Vacuum
Age	Amount of Drum Submergence
Temperature	Drum Speed

Viscosity
Compressibility
Chemical Composition
Nature of Solids

Degree of Agitation Filter Media Prior Conditioning of Sludge

One of the first attempts to dewater a lime treated acid mine drainage sludge by vacuum filtration was by Rummel (WE-078). Using the conditions of 3.2 square meters filter area of special nylon, 20 sec. drying time, and 0.6 atm vacuum, a cake was obtained with 23% solids; the original solids content was 0.6%. Sometimes, a dense impermeable cake is found that blocks the filter so that liquid flow is impeded. Filter aids can be added to the sludge slurry or as a precoating to the filter surface.

When vacuum filtration was applied to various pilot plant limestone sludge samples in TVA laboratories, 55-70% solids contents were achieved (SL-034). Original solids content and sulfate/sulfite ratio were not reported. Typical filtration rates employed were 2000-2200 lit/hr/m² (50-55 gal/hr/ft²). These results compared favorably with 38% solids obtained on settling alone. Considerable problems were encountered, however, because of the thixotropic nature of the sludge (EL-030). When the vacuum was released, the filter cake rewatered. Also, cracks formed in the filter cake in early stages of filtration which prohibited further dewatering. A third problem of difficult removal of the cake from the filter cloth may possibly be eliminated by air blast discharge.

Thermal Drying

Thermal drying of sludges is accomplished by the introduction of hot gases to remove the moisture from the solid. The four types of dryers used are flash, multiple hearth, rotary drums, and atomizing spray dryers. All of these units are capable of drying wastewater sludges to less than 10% moisture. However, due to the high fuel requirement thermal drying is economically unattractive compared to other methods. A range quoted for the capital and operating costs for a heat drying sewage sludge treatment is \$28-44/dry metric ton (\$25-40/dry ton) (WE-078).

Koch Engineering Company currently markets an SO_2 /fly ash control process involving a unique sludge dehydration operation (EB-003) in conjunction with a wet limestone or other alkali scrubbing system. The clarifier underflow having a typical solids concentration of 30% is pumped to the dehydrator where atomization occurs via a unique apparatus. The atomized slurry passes downward concurrently with the hot flue gases (~149°C) through the unit. The water content of the waste is reduced by 90-95%. The dry powdered solids are removed from the bottom. Fly ash is also removed along with the scrubber solids in this process. Figure 1 is a process diagram for a Koch limestone scrubbing system.

3.1.2.2 <u>Sludge Fixation</u>

Sludge fixation is the chemical and physical stabilization of sludge or sludge/fly ash mixtures. The intent of the processes is to convert the waste to a non-toxic, load-bearing material via chemical reaction and, in some cases,

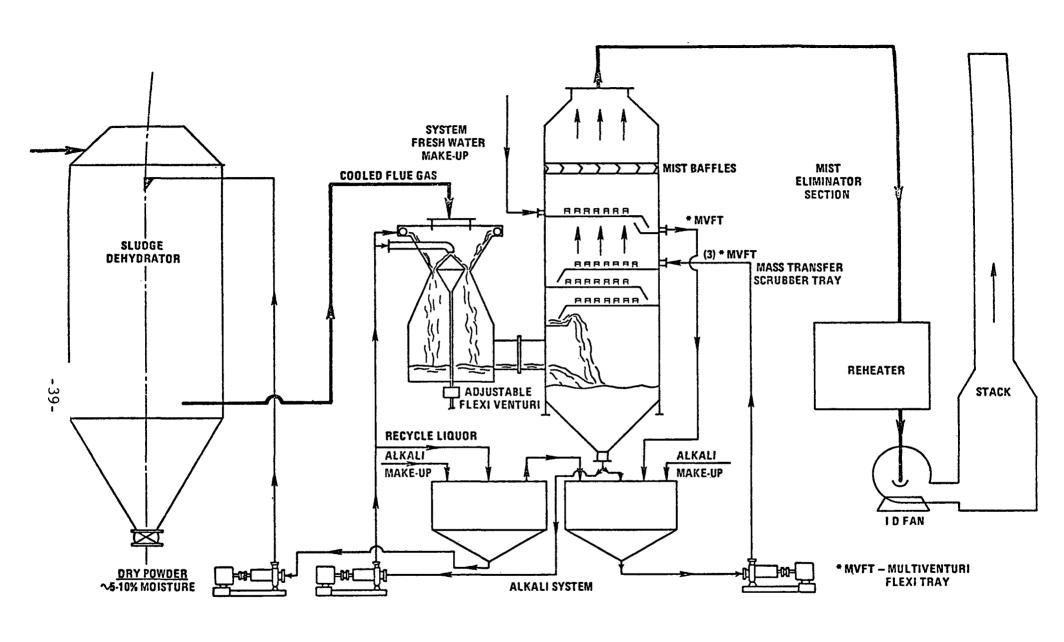


FIGURE 1 - FLY ASH - SO₂ EMISSION CONTROL SYSTEM (from EB-003)

aggregate addition. Chemical fixation of scrubber sludge and related materials is currently under development by several commercial groups including Dravo Corporation, I. U. Conversion Systems, Inc., Chicago Fly Ash, and Chemfix Corporation. mation available regarding the chemical and physical nature of lime/limestone scrubber sludge indicates a need to investigate potential stabilization techniques. Quantitative data describing various properties of scrubber wastes are presented in other sections of this report. Basically, these data seem to indicate a tendency for untreated, dewatered sludge to rewater upon contact with an aqueous environment. In addition, leaching and permeability features of dried sludges pose potential environmental hazards. The ability of proposed fixation techniques to prevent rewatering and leaching from treated sludges is under investigation. The current status of the fixation techniques now being marketed is described here.

I. U. Conversion Systems, Inc., offers several fixation processes based on the pozzolanic reaction between fly ash and lime (MI-084). Poz-O-Pac®, the original process on which sulfur oxide sludge fixation technology was based, has been industrially applied to the stabilization of fly ash for production of structural materials. Three basic chemical reactions are involved: (1) the reaction between the fly ash silica and hydrated lime to form cementitious hydrated calcium silicates, tobermorite; (2) the reactions between soluble salts present in fly ash with lime and the alumina content of fly ash glass; and (3) aggregate addition resulting in mechanical support.

Poz-O-Tec * is a commercial process for the stabilization of fly ash using sulfur oxide sludges in addition to

^{*}A service mark owned by I. U. Conversion Systems, Inc.

The chemistry is comparable to that describing portland cement technology. Calcium sulfate reacts preferentially with calcium aluminates or calcium ferrites resulting in hydrated calcium sulfoaluminates (ettringite) or sulfoferrites, respectively. The cementitious reactions which take place in the Poz-O-Pac® process also are an important feature of the Poz-O-Tec* process. Sulfite ion, introduced in large quantities as magnesium sulfite or calcium sulfite in the sludge, acts as a catalyst in the cementitious reactions. Addition of aggregate may or may not be required, depending on the characteristics of the starting materials and the desired strength of the product, referred to as Sulf-O-Poz®. This product is primarily a disposal material, but in some instances could be used as a structural material in land reclamation projects, structural embankments, etc. after a couple of weeks of curing (FO-018). Further processing of Sulf-O-Poz® is another alternative; utilization of the treated sludge as synthetic aggregate or road base material is then possible.

The tail end process itself can be retrofitted to existing power plant facilities. Application to oil-fired systems is not feasible, however, since availability of fly ash is essential to the process. Conditions of relatively higher pH, as in lime systems compared to limestone, favor the reactions, although both types of scrubber sludges can be treated by the IUCS process (AE-007). The presence of soluble magnesium compounds introduced as dolomitic limestones is claimed to result in faster, stronger reactions because of the higher sulfate solubilities.

 $^{^{\}star}$ A service mark owned by I. U. Conversion Systems, Inc.

The initial step in the process involves dewatering of the sludge by one or more of the techniques discussed in the preceding section. If fly ash is collected dry, addition to the sludge at this stage aids in the dewatering. If collection is by a wet method, the fly ash slurry may be introduced into the primary dewatering device. The sludge/fly ash mixture is then conditioned with make-up additives which may include additional lime, limestone, fly ash, bottom ash, other sulfur oxide salts, and optional aggregate or other waste products. The output from the mixing and conditioning device is suitable for utilization as a stabilized fill material. The flow diagram for this process is shown in Figure 2. To date, this process has not been applied to a flue gas desulfurization system, but extensive bench-scale testing of that application and the fixed product is currently being performed in the IUCS laboratories.

The economics of the fixation process offered by IUCS have been recently presented (MI-084). Because of the many factors influencing the actual costs that would be incurred by a power plant utilizing this system, the estimated cost cannot be considered typical. In addition, IUCS is not presently disposing of scrubber sludge on an industrial level; therefore, actual cost figures are not available.

Those factors affecting the cost of this or any fixation process are given below:

- annual tonnages to be handled by the conversion process,
- new boiler installation versus existing facilities,

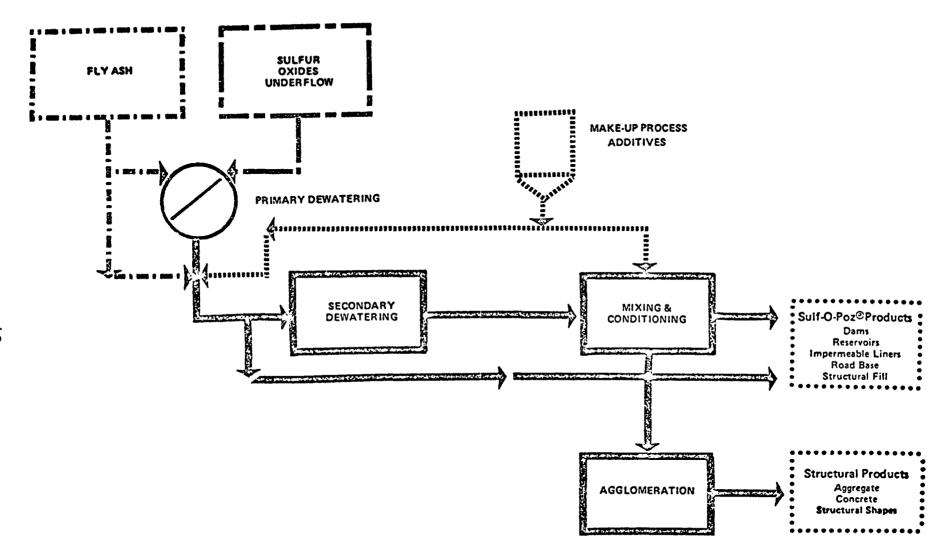


FIGURE 2 - SCHEMATIC DIAGRAM OF POZ-O-TEC* PROCESS
(From MI-084)

- the type of equipment selected for fly ash removal — for example, electrostatic precipitators versus wet scrubbers,
- the chemical analysis of coal sulfur,
 CaO, and ash contents,
- location of plant on-site versus offsite,
- transportation costs to and from conversion plant,
- redundancy factor duplication of equipment versus emergency holding basins, etc.
- type of scrubber limestone versus lime,
- · acquisition and cost of land, and
- type of end-product selected.

Based on estimates for newly installed plants in the range 1000 - 2000 MW, burning coal with 3-4% sulfur and 10-15% ash content, and incorporating a lime scrubbing system, the cost of sludge disposal is estimated to be \$1.65 - 2.76 per dry metric ton (\$1.50-\$2.50/dry ton) to convert the sludge to a disposable Sulf-O-Poz® material. This is equivalent to 7.9-13.9¢/108kg-cal (2-3.3¢/108BTU). This includes the cost of chemicals and process services, but not a hauling charge which is a major factor.

The Chicago Fly Ash Company also markets a sulfur oxides sludge fixation process based on quicklime/fly ash

addition (OB-005). They are currently working with Commonwealth Edison and the University of Illinois to dispose of the sludge generated by a limestone wet scrubbing system installed on a 163 megawatt unit at Will County Station (GI-017, GI-030, ST-117, The spent scrubber slurry presently receives dewatering treatment by clarification. Possible secondary treatment, vacuum filtration or thermal disc drying, is being considered to reduce the volume of sludge requiring fixation. Clarifier underflow is pumped to a pond, then to a loading station where the additives and sludge are blended to produce a stable landfill material. For every 1000 pounds of settled sludge, 100 pounds of fly ash and 50 pounds of lime are added. If higher water content is present, the proportion of additives required goes up rapidly The treated sludge (50% solids) is transported by cement (GI - 033). truck to an on-site sealed basin about one-half mile away. An off-site location is planned for the future. At the present time, this fixation process results in physical but not chemical stabilization of the sludge (GI-033). The leachate does not meet Illinois water standards which state that any water entering an aquifer cannot be of lower quality than water removed from it.

A Chicago Fly Ash spokesman quoted a cost of \$16.5/ metric ton (\$15/ton) on a dry solid basis for their process (OB-005). Additional economic information associated with this disposal method can be derived from estimated operating and capital investment costs reported by Will County. A utility spokesman has recently estimated the annual costs for the disposal system as 1.1 million dollars in addition to the initial capital investment of 1.7 million dollars (GI-017). The annual cost included a sludge disposal figure of \$823,000 which is equivalent to \$7.70/metric ton (\$7/ton) of sludge (dry basis), \$1.68/metric ton (\$1.52/ton) of coal, or 30.2¢/kg-cal (7.6¢/10°BTU). Entailed in the sludge disposal figure are costs for operating the sludge disposal plant, maintenance, hauling, and landfill. Actual costs

incurred on this project, however, are reported to be as high as \$17.10/ton of dry sludge (GI-033). Costs possibly may be reduced in the future to \$12/dry ton. This figure appears relatively high compared to the price quoted by I.U. Conversion. This situation is typical, however, in that the Chicago Fly Ash operation depends on a labor intensive trucking scheme in a congested area. This accounts for the relatively high cost in this specific application.

Dravo Corporation also offers a chemical fixation process for lime/limestone scrubbing waste products (SE-066). Much of their technology has been developed using sludge samples obtained at a pilot-scale lime scrubber operating at Duquesne Light Company's Phillips Station; sludge from additional sources has also been examined. The testing of their process has involved basic chemical and engineering evaluations of the sludge and treated product on a bench-scale level; they are currently under contract to Duquesne to dispose of their lime sludge. chemistry of the process has not been revealed because of current patent applications on the additive. The amount of additive required, however, is approximately 3-5% by weight of sludge solids. It is reported that following chemical addition to the settler underflow, the sludge can be pumped for 6 to 60 miles to a disposal site, preferably an area which can be dammed up, where the setting up takes place underwater. The supernatant can be drained off. Dravo has observed wide variations in sludge behavior even under controlled operating conditions (AE-006). variances have not been explained by either total chemistry or sulfite/sulfate ratio. Polyelectrolyte addition is being investigated to control these phenomena. The economics associated with this process includes an additive cost of less than \$19.8/ metric ton (\$18/ton). Dravo offers a complete package for sludge disposal. If a pumping operation is selected, the cost of the environmental impact statement preparation is estimated to be

\$500,000. Design of the system would be \$1-1.5 million, while the cost of the process itself would run \$12-13/dry metric ton (\$11-12/ton) according to Duquesne figures. Dravo, however, claims that the process cost would be considerably lower, depending on the pH of the sludge (LO-070). If the sludge is to be treated and stored at the plant site (i.e., no pumping operations) three settling ponds are required. The cost of sludge disposal in this case is \$1-3/ton of wet solids (35-40% solids) for a 1000-2000 MW facility. This figure does not include pond construction or equipment costs.

Chemfix Corporation markets a proprietary fixation process for conversion of various industrial sludges to stable landfill using at least two inorganic chemicals, one liquid and one powder. Little information is available on the chemistry of the system, although one source reports that "lime and silicates apparently are not used" (TR-026). Polyvalent metal ions react with Chemfix process chemicals resulting in a stable insoluble, inorganic compound within three days, although gelation time can vary with the system being treated. Certain species, including chlorides, monovalent cations, colloidal material and some organics, cannot be fixed by this treatment. This aspect, however, will be dealt with in a later section of this report (Section 3.1.2.3). At present, Chemfix is not working on an industrial scale with any utilities on scrubber sludge disposal although it has been applied to other types of problems. In one commercial operation, up to $380,000 \ \ell$ (100,000 gal) of sludge per day were treated (SO-048) at the Jones and Laughlin Hennepin Works. This involved treating the contents of a 19,000,000 ℓ (5 x 10 6 gal) lagoon. Completion of the job was accomplished in 21 days, ten-hour shifts. At Ford's Lorain assembly plant, 208,000 & (55,000 gal) per day of an industrial sludge containing toxins associated with painting operations has been periodically converted to a solid disposable landfill

material at an annual cost of \$100,000 (TR-026). On the order of four million liters per year are treated.

The price range quoted by Chemfix for their services is $0.51-2.6c/\ell$ (2-10c/gal) or on the average of $1c \ell$ (4c/gal) for a sludge of high solids content (TR-026). This figure does not include costs associated with hauling the fixed material to an off-site landfill.

Comparative evaluations of several of these processes are currently being planned or carried out in the laboratories of Aerospace Corporation under contract to EPA (Contract No. 68-02-1010) and in an independent study by Combustion Engineering, Inc. Aerospace plans to have sludge samples from four different power plants conditioned by at least two commercial processes. Testing of the treated samples will then be performed by Aerospace to determine the following characteristics:

- soluble components
- permeability
- water retention
- compression strength
- bulk density
- · detoxification assessment, if appropriate.

For each of the above processes, it is claimed that soluble components are immobilized in the treatment process. Specific data to support these claims have been reported by

I. U. Conversion Systems whose results are discussed in Section 3.1.2.3. Chemfix Corporation has furnished leachate analyses to Radian for specific treated sludges. These results are also presented in Section 3.1.2.3. No data from Dravo Corporation or Chicago Fly Ash was available for release at this time.

3.1.2.3 <u>Water Pollution Potential and Control for Landfill</u> Disposal

Disposal of sludge generated by lime/limestone scrubbing systems in landfill sites creates two potential areas of water pollution, leachate to groundwater and runoff to surface water. Careful evaluation of available research results associated with both runoff and leachate must be made in order to assess any potential environmental hazards which may exist. In this section, information pertaining to factors of water pollution and effect of chemical and physical properties of stabilized scrubber sludge/fly ash mixtures are discussed. Also presented here are possible control measures which have had application in disposal of sludge or other solid waste materials.

Leaching Aspects of Landfills

In order to predict leachate characteristics of a landfill, it is first necessary to describe the general features of water movement and geological considerations for this disposal method. Due to the recent surge of ecological interest in sanitary landfills utilized for solid waste disposal, there is an abundance of information available. Emrich's review of research in this field presents an overall view of progress in the following areas (EM-003):

- · leachate generation
- · chemical characteristics of leachate
- movement of water in a landfill
- effects of topography, geology, soil, and groundwater on leachate
- · leachate or landfill management.

This section will present a discussion of landfill leachate in general with specific reference to formation, nature, and movement of leachate generated by lime/limestone scrubber wastes.

The first consideration when looking at the potential impact of landfill leachate is the volume of leachate which will be produced. This is a direct function of the amount of water reaching the landfill. There are two possible sources of this water: rainfall and naturally occurring subsurface flow through the landfill site. This second situation occurs when the landfill extends below the existing water table. Climate obviously will determine the rainfall. In humid areas leachate will be generated in a relatively short period of time; leachate formation may be delayed for years until field capacity is reached, however, in semi-arid and arid regions (EM-003). In general, the field capacity of a landfill is the water that can be retained indefinitely against gravitational force.

Subsurface flow is a natural phenomenon which can seriously interfere with safe operation of landfills in two ways. First, it is a source of additional volume of potentially harmful leachate. The second consideration is that it can

serve as a direct means of groundwater contamination. Prevention can be effected by thorough geologic study of the site beforehand and, if needed, installation of rerouting devices for the groundwater flow.

In a similar vein, coverage of the landfill area when complete will greatly reduce, if not eliminate, the amount of leachate produced. This aspect will be discussed in a later section dealing with potential pollution control measures.

Infiltration and permeability characteristics of the landfill material determine the relative amounts of runoff versus leachate as well as the leaching rate. Minnick has looked at the effect of aging on permeability of fly ash stabilized with lime (Poz-O-Pac®) and fly ash stabilized with sulfur oxide sludges in addition to lime (Poz-O-Tec*) (MI-084). As shown in Figure 3, a great reduction in permeability of fly ash mixtures can be achieved by inclusion of sulfur oxide sludges. In terms of the subject of this report, these results indicate not only the low permeability values of the fixed scrubber sludges (~10⁻⁷ cm/sec after 7 days of curing at 100°F or 38°C), but also the relatively great reduction in permeability compared to freshly prepared sludge/fly ash mixtures. This reduction is on the order of two orders of magnitude. More specific data obtained with samples of sludge stabilized by I. U. Conversion System's process is presented in Table A22. These data were measured using standard falling head permeability procedures.

Dravo Corporation reportedly has obtained permeability values of $2 \times .10^{-5}$ cm/sec for sludge conditioned in their laboratories with 3% additive (AE-006). This is compared to high quality clays having permeation values of 10^{-7} to 10^{-8} cm/sec versus fly ash for which a representative range is 10^{-3} to 10^{-3} cm/sec.

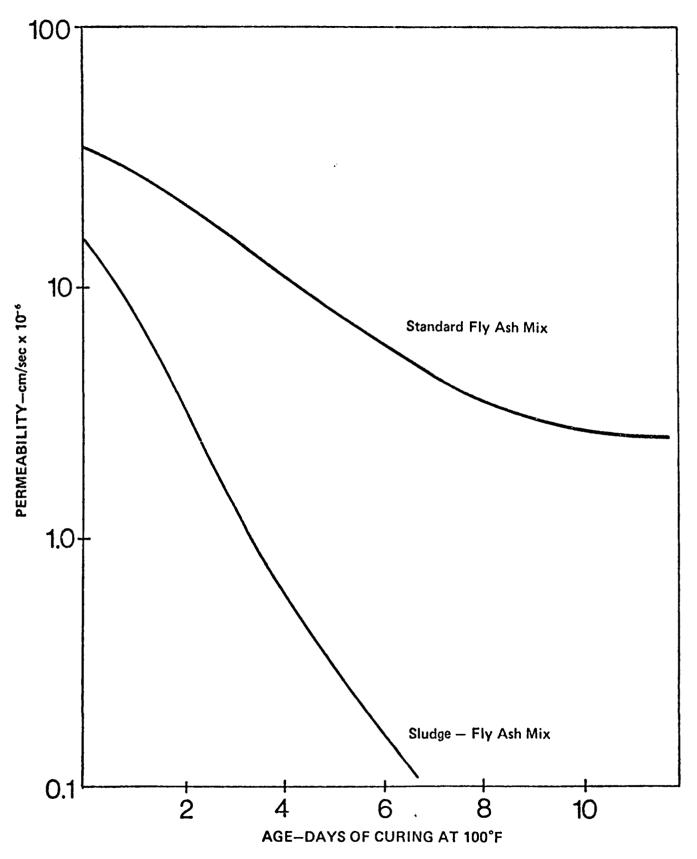


FIGURE 3 – Comparison of Poz-O-Pac® and Poz-O-Tec* permeability values. (MI - 084)

Minnick has presented analytical results obtained by atomic absorption analysis of leachable ions on selected materials subjected to the Poz-O-Tec* or Poz-O-Pac ® process (MI-084). The tests were conducted by shaking 500-gram test specimens for 48 hours in two liters of distilled water. The results of those studies are shown in Table A23. When leachate from materials treated by Poz-O-Tec* process were compared to Federal specifications for drinking water standards, only manganese greatly exceeded the limits. It was noted that materials not treated by either stabilization process experienced much greater leaching phenomena, thus indicating the effectiveness of this type of chemical fixation. In Table A23 the decrease in total dissolved solids with aging for the Dulles cylinder is noteworthy.

The Chemfix process, although not applied to sulfur oxide sludges, has been shown to lack ability for some sludges to retain several elements, including chloride, cyanide, and hexavalent chromium species (TR-026). One source reports that a test of leachate from a Chemfix solid contained 1,000 ppm chloride, four times the permitted level in drinking water (F0-018). Chlorides are of special concern in lime/limestone scrubbing wastes because of their high solubility and unavoidable build-up during closed-loop operation. The presence of very high concentrations of this anion could have an appreciable effect on trace metal ion concentration in scrubber liquors and sludge leachate. This potential pollution aspect requires further investigation.

A sludge sample from an Eastern coal-burning power plant controlled by a limestone scrubbing system was Chemfix treated (CO-123). Analyses of the raw untreated sludge and leachate from the fixed sample were performed. The results

as shown in Table A24 indicate that the concentrations of reported toxic elements and ions were reduced in most cases to less than 0.10 ppm. Copper and lead concentrations also decreased to this value after the first leachate portion.

Runoff Considerations for Landfill

I. U. Conversion has performed tests to determine the extent of dissolution of species associated with fly ash-stabilized sulfur oxide sludges (MI-084). The experiments were conducted by allowing two liters of deionized water to flow over the fixed samples and then subsequently collected.. Results of atomic absorption analyses of this runoff were reported as shown in Table A25. They were interpreted as providing a preliminary basis for the effectiveness of the fixation process's ability to tie up soluble species within the lattice complexes.

<u>Preventive Measures for Potential Pollution from</u> Landfills

Methods available to prevent contamination of surface and groundwaters include landfill sealing, coverage, and provision of drainage to divert naturally occurring surface or groundwater flows around the landfill.

Landfill sealing is very similar to the practice of pond lining discussed in Section 3.1.1.2. The sealant can be any impermeable material such as an asphalt-membrane recently tested at a site near Tullytown, Pennsylvania (RE-071, LA-079). Many other potential lining materials have been tested in bench-scale and experimental plot arrangements. A few of the more promising of those tested included:

- 10% bentonite (Wyoming clay used for mud drilling)/90% soil
- 10% bentonite/90% sand
- 10% red mud slurry (a bauxite residue)/
 90% soil
- · 10% latex/90% soil
- 30% asphalt emulsion/70% soil.

In an arrangement where a landfill liner is used, the leachate is trapped at the bottom. It can then be collected and subjected to water treatment, if necessary, before release to the surrounding area.

Interception of subsurface flow is achieved by placement of drains upstream of the entire area of the landfill. These cut-off drains should be placed at a depth a few feet below the bottom of the landfill to keep the groundwater level low as well as to provide hydraulic gradient for drainage (SA-103).

To prevent infiltration from surface flow, two measures can be taken. One involves providing vertical gravel or stone paths extending below the level of the bottom of the landfill through which surface and/or groundwater can quickly drain. The second approach involves using a cover material. This may be a natural material such as clay or clay loam, or an artificial membrane. If an impermeable cover is employed, precaution must be taken to allow release of gases to the atmos-

phere. In some instances, carbon dioxide produced in a landfill has been observed to contaminate groundwater with additional hardness.

3.1.3 Other Disposal Methods

Several other possible options are available for disposal of air pollution control system sludges although they are not under investigation to the same extent as landfill and ponding. These alternatives involve direct deposit of the waste below the surface, either in deep injection wells or in subsurface mines.

Deep mine filling has been used for the disposal of power plant ash (HA-158). The ash is sluiced into the mine through boreholes. Normally, gravity is sufficient to create a flow into the mine. Pumps and additional boreholes were provided in case of hole plugging or increased friction losses. A dewatering sump and a settling basin were formed by constructing dams across the mine flow. Overflow from the settling basin flows to the sump from which it is pumped to an above-ground basin. This type of approach is not directly applicable to disposal of lime/limestone scrubber sludges for several reasons. First, the viscosity of this waste is such that it is probable that it would not spread laterally throughout the mine disposal area. Secondly, the settling characteristics have been shown to be poor; ready solid/liquid separation is not expected (Section 2.2). This would eliminate the attractive features of a mine subsidence operation in that very little geological support would be provided by the water pollution aspects. Possibly the last two foreseeable problems could be avoided or reduced by a fixation treatment. gation of this approach may be worthwhile to those utilities

to which abandoned deep mines are available as a possible disposal site.

Reclamation of strip mine areas with waste sludge is another possibility. This could be viewed as a specialized landfill operation; as was discussed in the preceding section, it is not yet certain whether or not pretreatment of the sludge will be required for strength development and to prevent environmental contamination. The benefits of this type of disposal are obvious, however, if shown to be a feasible approach. In addition, land availability would not be a problem in many areas of the nation, including the State of Ohio where strip mining is a large industry, especially along the eastern and southeastern borders. Strip mine reclamation with fly ash has been in practice for many years now, much of it under the development of the Bureau of Mines. Additional development is needed for utilization (disposal) of scrubber sludges in this capacity.

Another alternative to ponding and landfill is deep well injection. This method has been utilized by a number of industries seeking permanent disposal of hazardous waste materials. There is no information, however, concerning its potential use as a scrubber sludge disposal technique. The high solids content of the sludge probably would cause rapid plugging of the subsurface strata, resulting in decreased permeability and continually diminishing injection rates. Possibly some very permeable formations exist where this would not occur. Although this method offers another alternative to the sludge disposal problem, it is not regarded as a highly feasible solution.

3.2 Sludge Handling and Transport

The handling operations involved in disposing of scrubber sludge may include one or more of the following: wet sluicing of sludge and/or fly ash; trucking of ash and other fixation additives; trucking of sludge to landfill site; use of conveyor belts for sludge transport between dewatering, treating, landfilling, and/or trucking facilities; barging; and rail transport. Each of these is briefly described below with emphasis placed on any aspects possibly associated with air pollution control system sludge.

Transport of waste scrubber sludge to the ponding site can be carried out by sluicing operations, i.e., piping the slurried solids. This method is also being considered for transport of sludge to the fixation site. Individual sludge properties such as viscosity, velocity, temperature, composition, particle size, and solids concentration affect the pumping characteristics of the material. Also of major concern is the distance to be covered. Special problems specifically related to sulfur oxide sludges such as corrosion or erosion potential also require investigation. Dravo Corporation is investigating the transport of fixed sludges to the disposal site by pipeline.

In general, the transport of solids in pipes depends on the use of a carrier fluid to transmit pressure from the pump or compressor to the solid being moved. The viscosity of the material greatly influences the transport characteristics. Viscosity is a physical property defined as the cohesive force between particles of a fluid that cause the fluid to offer resistance to the relative sliding motion between particles. It is a measure of the resistance to flow. This physical property has been determined for a number of individual scrubber sludges; the data were presented in a previous section of this report (Section 2.2). Specific characteristics such as thixotropic or rheopectic behavior unique to some scrubber sludges are related to viscosity and therefore will influence sluicing operation parameters. For instance, sludges with high sulfite composition exhibit thixotropic behavior as described in Section 2.2. This observed loss of viscosity with stirring would result in lower head loss at constant velocity of the fluid. A different sludge, however, has been shown to exhibit rheopectic behavior. This would tend to have an adverse effect on pumping operations. Therefore, the physical nature of the sludge being transported must be known.

The critical velocity for a particular sludge must be determined since it is the flow velocity at which solids are most economically moved for a given pipe size and sludge. This velocity will occur somewhere in the turbulent flow region; i.e., the region in which particles may move in any direction with respect to each other.

Other technical aspects of pipelining of sludge requiring consideration prior to design of a system are materials of construction and possible use of pumping aids. Transport can be accompanied by erosion problems due to the physical nature of the solids. In many installed lime/limestone systems, much of the piping, blades, and pumping equipment used to transport slurries are rubber lined to protect against the abrasive properties of the slurry, especially in pipes carrying sludges of higher solids content.

The use of long-distance piping systems is increasing rapidly since the demonstration of technical and economic feasibility. Table 4 summarizes the commercial applications which have been installed in recent years.

Truck transport of dry materials such as fly ash, lime, and aggregate is an established practice in various industries. Major considerations in employing this handling method are proper equipment for loading and unloading, and control of fugitive dust. Dry materials (lime, e.g.) are most often handled by pneumatic sluicing systems which can be designed to load the material directly to the truck or hopper. Pneumatic unloading systems which blow the material from the trucks are employed to handle materials which do not flow freely. Pneumatic systems are not necessary, on the other hand, for relatively free-flowing materials. In this case, the unloading equipment requirements depend on other physical characteristics of the material.

The second consideration involved in truck transport of dry materials is control of fugitive dust, i.e., wind-blown dust. Proper precautions must be taken in order to avoid air pollution problems associated with this feature. Again, the extent of the potential problem depends on the physical characteristics of the material being handled. Usually properties associated with materials posing this hazard are small particle size and low density. Although this is unlikely to be a problem with scrubber sludge due to its high water content, conditioning of fixation process additives such as fly ash or lime would be necessary.

TABLE 4
SUMMARY OF COMMERCIAL SLURRY PIPELINES
(TH-041)

		Location	Material	Length (miles)	Diameter (inches)	Throughput (million tons per year)	Solids Specific Gravity	Weight (% Solids)	Years in Operation or Status
	Consolidation Coal	Ohio	Coal	108.0	10	1.30	1.40	52.0	6*
	American Gilsonite	Utah	Gilsonite	72.0	6	0.38	1.05	46.0	11
	Rugby Cement	England	Limestone	57.0	10	0.70	2.70	61.0	5
	Columbia Cement	Columbia	Limestone	9.2	5	0.35	2.70	55.0	25
	South African Companies	South Africa	Gold Tailings	21.5	6 & 9	1.05	2.70	50.0	14
	Savage River Mines	Tasmania	Iron Concentrate	54.0	9	2.25	4.90	60.0	2
-61-	Black Mesa Pipeline, Inc.	Arizona	Coal	273.0	18	5.70	1.40	50.0	In Start-Up Phase
	Hyperion Wastewater Treatment Plant	Los Angeles	Digested Sewage Sludge and Effluent	7.5	22		1.80	1.0	11
	Mogden Wastewater Treatment Plant	England	Digested Sewage Sludge	7.0	12		1.80	4.0	33
	Easterly Pollution Control Center	Cleveland	Raw Sludge	13.0	12		1.80	2.5	32

^{*} Commercial operation ceased in 1963 for non-technical reasons. Now maintained in standby condition.

Transport of sludge to a landfill site via truck is one of the most feasible approaches being considered by utilities if off-site disposal is used. The results of one study are available at this time (TA-040). Combustion Engineering transported 68 metric tons (75 tons) of waste (50% sludge, 50% ash) from the limestone scrubber at Kansas Power and Light's Lawrence facility to Dulles Airport in Washington, D.C., a distance of approximately 2100 km (1300 miles). Two types of vehicles, flatand round-bottomed trucks, were employed in order to compare the effect of various features on handling characteristics. to loading, the untreated sludge had been stored in a settling pond at the utility site for six months. It was dredged up and allowed to drain for 24 hours before loading. At various intervals during the non-stop trip measurements and samples were taken. No leakage of sludge was observed although excess water drained from the tail gate while on the road. Unloading problems were encountered with the flat-bottomed trucks; complete removal of the sludge necessitated manipulation with a backhoe. The sludge slid out readily, however, from the round-bottomed trailers.

Conveyor belts and related bucket elevators are potential modes of transport for dewatered sludge over short distances. Potential areas of use include conveying of dewatered solids to a fixation facility, lifting of wastes to hoppers or mixing devices, and transport of fixed sludge to landfill sites. The water content of the sludge is the major factor determining feasibility of this application. If the nature of the sludge is such that water drains in large amounts, precautions such as installation of troughs below the conveyors must be taken to avoid potential water pollution problems.

Other handling aspects which would be mentioned in this discussion are alternate methods of transporting the waste from the scrubber site to the ultimate disposal site. Encompassed in this category would be barge and rail. Both would be feasible only in unique situations where geography and surrounding environment would permit such application.

The economics of solids handling by sluicing or piping operations depends mainly on two factors: amount to be handled and distance to be covered. One source, in comparing the economics of piping versus truck transport, stated that 80 km (50 miles) should be considered the cut-off distance. For distances greater than 80 kilometers piping appears more economically attractive (BO-075). Thompson reported total pipeline transport costs (including power, labor, supplies, and capital charges) to range from \$1.76 per dry metric ton of sewage sludges (3.5% solids) for a 40 kilometer, 820 metric tons/day system (\$1.60/ton for a 25-mile, 900 tons/day system) to a maximum cost of \$22 per dry metric ton for a 160 kilometer, 91 metric tons/day system (\$20/ton for a 100-mile, 100 tons/day system) (TH-041).

The results of another survey in which off-site disposal costs were reported gave figures in the range of \$0.01 - 0.10/m³·km (\$0.05 - 0.50/1000 gal·miles) for pipeline conveyance of brines and sludges (BU-087). These costs did not include fees charged by the receiving agency. The authors of the report concluded that pipeline conveyance is the most economical mode for quantities in excess of 100 cubic meters (26,000 gallons) per day irrespective of distance. Over long distances it seems reasonable to expect that piping would be more economical than trucking for smaller quantities. For

smaller volumes and short distances, trucking or rail becomes more economically attractive. In this case distance should be the basis of selection; trucking for distances shorter than 35 miles (50 km) and rail haul for longer distances.

3.3 Land Reclamation Aspects of Disposal Sites

Certain aspects of land reclamation following abandonment of a landfill site or dried up.pond used for scrubber sludges may lead to potential problems. These aspects may be assessed by examining the engineering, physical, and chemical natures of treated and untreated sludge.

At the present time no attempts have been made to reclaim land committed to scrubber sludge disposal. However, Florida's phosphate mining industry has successfully accomplished several full-scale reclamation projects. These involved conversion of the ponding, mining and disposal areas to recreational areas and residential subdivisions. The work done in this area is described in Section 3.3.4.

3.3.1 Rewatering Characteristics

One consideration is the tendency of dried scrubber sludge to absorb water with which it comes in contact. As discussed in previous sections of this report, sulfur oxide sludges are relatively difficult to dewater. One sludge sample was observed over a period of several months during which time little or no settling took place after the first 48 hours. Preliminary results of one TVA study indicated that dry solids from a limestone scrubber sludge do not expand when submerged

in water or exposed to rainfall (SL-034). Drainability studies conducted by Aerospace, on the other hand, resulted in retention of enough water by dried Shawnee limestone sludge to return to its original water content. The calculated water retention for sludge with underdrainage was 51.7% (AE-007). Behavior of. chemically stabilized sludge samples is expected to be greatly improved although specific tests for rewatering potential have not been reported. A practical consideration in regard to rewatering is that for a thick layer of dried sludge, an accumulation of a few meters of rain might be required for rewatering. With proper design of the site plus some low permeability cover material (clay, plastic, or treated sludge) even untreated sludge might never rewater since the small amount of water collected during a rain should be lost by evaporation before the next rain.

3.3.2 Strength of Disposed Material

A second consideration in land reclamation of sludge disposal areas is the weight which can be supported by the site. This factor can be determined by measuring the pozzolanic strength, compaction strength, and penetration resistance of the throwaway product. The strength associated with any landfill or construction material is a function of composition, moisture content, and compacted density.

Untreated scrubber sludge has been shown to lack any appreciable degree of compressive strength based on studies performed by Aerospace on Shawnee and Mohave samples (AE-009). Compaction strength is measured by the resistance of wet sludge to penetration of a flat bottom ram, 1 cm in diameter. This parameter is used to evaluate the amount of weight which

could be supported by ponded sludge. Shawnee limestone sludge at 44% water content was found to support 320 kg/m^2 (0.45 psi). Sludge dried to 40% water possessed a higher compaction strength of 1500 kg/m^3 (2.2 psi). When compared to the stress required to support a normal person, 2100 kg/m^2 or 3 psi, both dried and wet sludge were judged to lack any appreciable degree of compaction strength (AE-008). More recent test results of Shawnee sludge dried to 30% water content, however, showed a substantial increase in strength ($24,000 \text{ kg/m}^3$ or 34 psi) (AE-009).

Pozzolanic strength determinations were made by applying compression strength at a constant strain rate to samples which had been cast in cylindrical molds and cured for a given time in a humid environment. This property was reported to vary as a function of water content. Testing was carried out with an Instron test machine using a cross-head speed of 0.05 cm/min (0.02 in/min). Results are shown in Table A26 (AE-009). Water content of the samples, however, was not stated.

Samples subjected to the I. U. Conversion Systems' fixation process have been tested for various strength characteristics (MI-084). The penetration resistance is a measure of the pressure that must be applied in kilograms per square meter to cause a penetration of 2.54 cm (1 inch) of a needle with cross sectional area of 1.6 x 10⁻⁵ square meters (1/40 square inch). The effect of aging on the strength of a Sulf-0-Poz ® composition was presented in graphical form (Figure 4). The results indicate that completion of curing occurs approximately 16 weeks after mixing. When 5 x 5 x 5-centimeter cubes of similar composition were tested for unconfined compressive strength, curing was completed much sooner (~6 weeks). Graphical display of results is shown in Figure 5. Individual data points obtained during bench-scale compressive

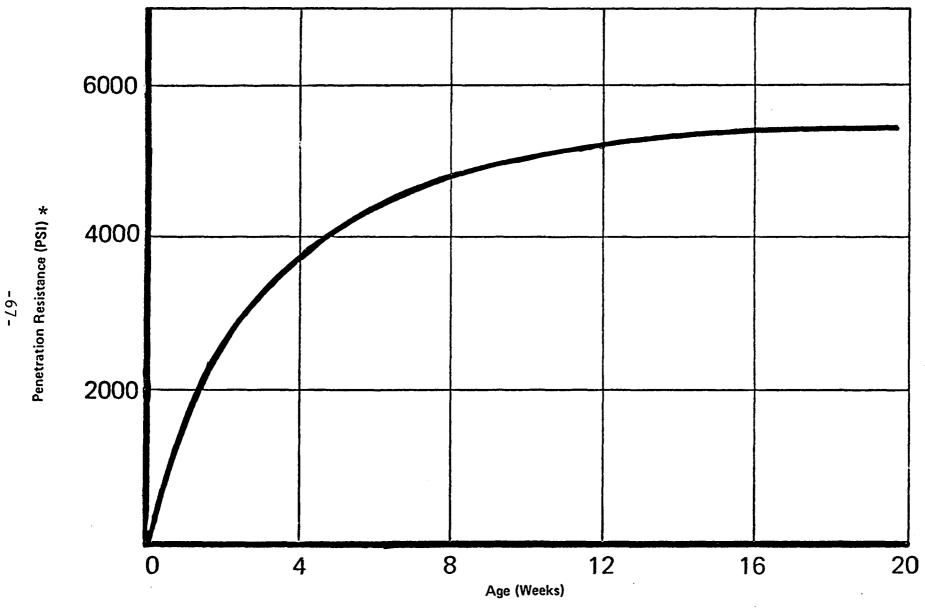


FIGURE 4 - Penetration resistance for a typical fly ash-calcium sulfate-lime mixture. (Fixed Sludge-- (from MI-084)

 $^{^*}$ One psi is equivalent to 703 kg/m²

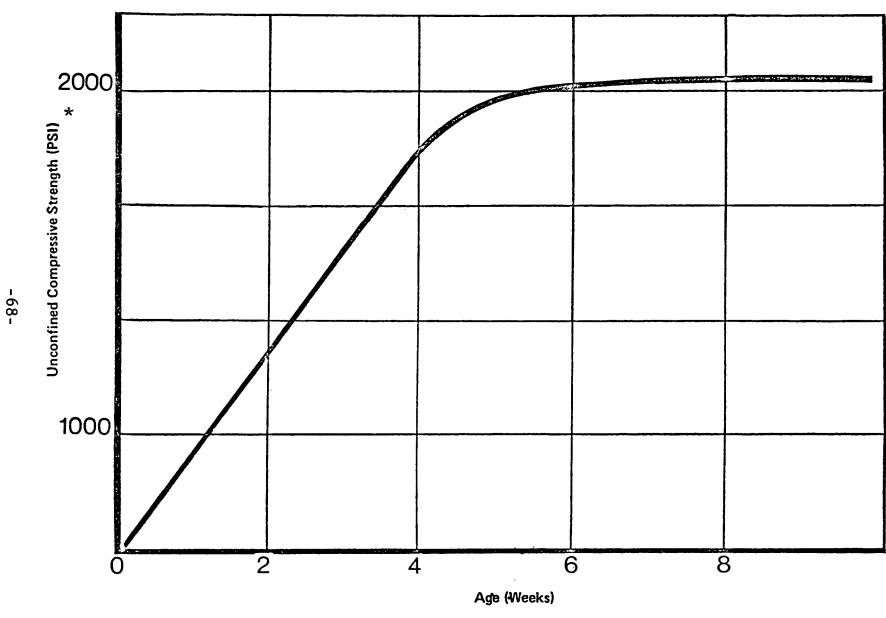


FIGURE 5 - Compressive strength for a composition similar to that given in Figure 4 Moisture content of composition is 35%. (Fixed Sludge) (from MI-084)

 * One psi is equivalent to 703 kg/m²

strength determinations of Sulf-O-Poz $^{\textcircled{0}}$ materials with moisture contents of ~20% are shown in Table A27. Also presented are the results of compressive strength determinations for field tested road base materials (Table A-28).

In addition to strength, another consideration in an engineering evaluation is structural integrity. Experimental data which can be used to describe this characteristic are dimensional stability measurements and field testing.

Untreated sludges reportedly have very poor dimensional stability. On exposure to drying conditions, shrinkage and cracking was observed (AE-006). 3.7% linear shrinkage was measured for Shawnee sludge. This was found to be a function of water content. This phenomenon can be prevented by addition of a pozzolanic material such as is involved in most of the stabilization processes now offered. I. U. Conversion has reported the results of behavior of Sul-O-Poz ® material molded into 2.5 x 2.5 x 25-cm bars and cured at 23°C (73°F) (MI-084). In each case, an initial slight expansion was observed; the degree of expansion leveled off within 3-4 weeks for low lime content samples and within 5-6 weeks for high lime samples, with respective overall increases in length of ~ 0.003 and 0.008 cm/cm. Field tests to date have produced good results with regard to structural integrity.

3.3.3 Support of Vegetation

An additional factor to be considered in reclamation of abandoned sludge disposal sites is whether growth of vegetation can be supported on the area. At the present time no studies are available directly concerning this aspect.

3.3.4 Related Experience in Land Reclamation

Florida's phosphate mining industry is effectively dealing with reclamation of mined-out areas and slime pits. Several types of solid wastes are generated from the mining practices. Phosphate rock slimes resulting from the initial washing process are generally handled as a 7% solids slurry of extremely fine-grained clays. This waste is typically disposed of by ponding, but settles only to 25% solids even after two years. Figure 6 illustrates a typical slime pond in operation. Mine tailings consist of non-phosphate sands which are separated from the phosphate minerals by a double flotation These tailings have proven very valuable in several capacities: mine fill, construction material for pond dams, and pond reclamation fill. In the first capacity great success has been achieved. Several abandoned mining areas in Florida have been converted to residential areas which support abundant vegetation. An additional benefit is the change in land contour resulting from the mining/reclamation activities; what was once extremely flat uninhabited land, is now esthetically contoured residential area.

A primary use of mine tailings is in the construction of dikes and dams for slime dewatering ponds. This practice has been employed for many years in the industry. The contents of the ponds are capable of supporting abundant water life. When filled some ponds have been successfully reclaimed as recreational areas such as parks and golf courses as shown in Figure 8 although they do not possess the engineering strength required for support of buildings. The reclamation is achieved by covering the slimes with a three to four foot layer of tailings. In Figure 7 the reclamation of a pond is shown in



FIGURE 6 - PHOSPHATE SLIME POND IN OPERATION



FIGURE 7 - A SLIME POND RECLAMATION OPERATION



FIGURE 8 - SLIME POND CONVERTED INTO RECREATIONAL AREA



FIGURE 9 - TYPICAL BY-PRODUCT GYPSUM DISPOSAL

progress. Although this has been demonstrated to be technically feasible, it is not always practiced because of the short supply of tailings which are more needed in dam construction applications.

In a related industry, the wet process phosphate manufacture, one of the main waste products is a fairly pure grade gypsum. Figure 9 shows how this waste is disposed of in huge gypsum piles, rising to sometimes a hundred feet and extending for miles. This material has been stockpiled for years with little effort to reclaim the disposal areas. Some effort has been expended to develop new commercial uses, although there is currently little outlet for the gypsum in this direction in Florida. Limited information is available on possible environmental hazards associated with this disposal technique.

This information is relevant to lime/limestone scrubber sludge disposal in several ways. First of all, the reclamation of slime ponds has proven the technical feasibility of converting a disposal site for a low solids, poor settling material such as scrubber sludge to a beneficial, life-supporting area. Secondly, the vast stockpiles of relatively pure waste gypsum indicate that potential marketing of scrubber sludge as gypsum in some geographic areas is highly unfeasible, particularly since the scrubber sludge in many cases will contain large quantities of fly ash. The fact that no environmental episodes have been reported from either properly constructed slime ponds or gypsum piles does not necessarily indicate that no hazards exist, but it does seem to indicate that no major problems are associated with either type of disposal.

3.4 <u>Commercial Utilization of Sludge</u>

The alternative to disposal of scrubber sludges is development of commercially applicable utilization processes. Numerous programs in this area have been conducted through government sponsorship and by industry alone. These are summarized in Table 5. In this section of the report different areas of utilization of lime/limestone scrubber sludge are discussed. First, those efforts are described for which technology has been demonstrated on a relatively large scale. Then an overview of other potential uses for which limited technology exists is given.

Combustion Engineering, in cooperation with the Research and Development Division of the Federal Highway Administration, studied the potential of several industrial sulfate sludges as highway construction materials (TA-040, BR-112). The major portion of a parking lot of the Dulles Airport in Washington, D.C., was paved with a mixture of fly ash, lime, and sulfate sludge from a hydrofluoric acid plant.

In another section a mixture of lime (3%, dry basis), SO₂ scrubber sludge (8%), fly ash (59%), and aggregate (30%) was tested as a road course material. The sludge was a 50% solids slurry obtained from Combustion Engineering's limestone scrubbing system at Kansas Power and Light's Lawrence facility. The paving mixture was placed in a seven-inch layer over a compacted subgrade, compacted to five inches, and sealed with a bituminous material to prevent water infiltration. During the construction period, weather conditions were especially wet. Consequently, neither the subgrade nor the paving mixture hardened sufficiently, and compacting operations were hindered. The sealant, which consisted of a material not usually used in this application, also failed

TABLE 5

SLUDGE UTILIZATION SCHEMES

I. FILLER MATERIAL

- A. Structural Fill
- B. Mine Void Fill
- C. Filler in Bituminous Concrete
- D. Waste Disposal/Sanitary Structural Land Fill

II. Pozzolanic Products

A. Road Base Course

III. Autoclave Products

- * Concrete Admixture (Structure and Products)
- * Fired Brick
- * Lightweight Aggregate

IV. Pressure Sintered Products

- A. Metal Coatings
- B. Pipes

V. Gypsum Products

- A. Plaster
- B. Wallboard

VI. Soil Amendment

VII. Mineral Wool

TABLE 5

(Cont.)

VIII. Mineral Recovery

- A. Lime
- B. Aluminum
- C. Iron
- D. Pozzolan (glass particles)
- E. Titanium
- F. Silicon
- G. Rare Elements

IX. Sulfur Extraction

- A. Sulfur
- B. Sulfuric Acid

X. Polluted Water Treatment

- A. Recovery of polluted streams, ponds, lakes
- B. Neutralization of Acid Mine Drainage and Polluted Waters
- C. Sewage Plant Treatment

to prevent seepage of moisture to underlying layers. As a result, the parking lot surface broke up in many spots and generally did not stand up to traffic as well as results of bench-scale tests had predicted. Despite these problems, however, the demonstration project served to firmly establish the feasibility of this utility scheme.

IUCS offers a process called Poz-O-Tec* to convert power plant scrubber sludge to stabilized structural fill material or to usable manufactured by-products. As described in Section 3.1.2.2, the process is based on technology of the Poz-O-Pac® process which is also a fly ash stabilization technique.

The product of the Poz-O-Tec* process, Sulf-O-Poz[®], can be used as a stabilized fill material. It possesses certain structural qualities permitting its use in some cases as structural embankments, land reclamation projects, and liners for ponds and reservoirs. Sulf-O-Poz[®] can be further processed to produce cementitious material of other compositions such as synthetic aggregate suitable for production of structural shapes, portland cement or asphaltic concrete. Sulf-O-Poz[®] may also be supplied directly for use as stabilized road base required in primary highways, airport runways, trucking terminals, and similar applications.

The engineering properties of Sulf-O-Poz® material have been described previously in this report. The characteristics are functions of the fly ash/sludge ratio and the lime and water contents. Poz-O-Tec* mixtures that have been placed in dams and reservoirs are expected to show little deterioration for many years. In the same fashion, these mixtures, when used for road base work, have proven to be superior to the Poz-O-Pac® compositions.

Gypsum is one of the solid by-products of the wet lime/limestone gas desulfurization process. This material can be recovered although the feasibility of doing so is limited by the amount of foreign material in the sludge, i.e., fly ash, unreacted lime or limestone, and calcium sulfite. Elimination of fly ash can be achieved by burning oil rather than coal or by installing efficient electrostatic precipitators upstream of the scrubber unit. Oxidation of sulfite to sulfate is currently practiced in Japan and is under investigation in this country as well. The fly ash elimination and oxidation processes result in a clean grade gypsum, CaSO₄·2H₂O, which is used in making wallboard, wall plaster, or as a cement additive for construction use. This approach has already been taken in Japan. one plant sulfite is oxidized to sulfate in special equipment. Similarly, sulfite oxidation equipment is being installed at the Mitsui Aluminum Plant in Japan. It was recently predicted, however, that the Japanese supply of gypsum will soon exceed the demand (AN-059). The economics of this utilization process may not be acceptable in the United States where there exist large natural sources of relatively pure, dry gypsum. Moreover, if an efficient precipitator is not employed, the dark color of gypsum due to fly ash and other impurities could be a significant problem for a potential gypsum market. The economics of the utilization are more favorable in the Chiyoda and Hitachi processes where the gypsum is manufactured from sulfuric acid and hence the oxidation step is circumvented.

The potential utilization technologies described up to this point are fairly well established in that they are either commercially practiced or have at least been successfully demonstrated on a large test scale. A list of less promising schemes which have been suggested are included in Table 5. Those marked with an asterisk were judged to be economically unfeasible

in a study conducted by Aerospace Corporation for EPA (Contract F04701-70-C-0059). The following were the chief factors making a particular scheme unattractive:

- need to dewater the sludge prior to utilization
- release of sulfur during a heating step involved in manufacture of product
- relatively low pozzolanic properties compared to ash alone
- inability to compete with less costly products.

Progress in several of the more developed technologies are described briefly below.

Autoclaved Products

The technology for autoclaved products was developed at the Coal Research Bureau, West Virginia University, under contract to EPA (CO-118). Three classes of autoclaved products employing lime/limestone scrubber sludge as the principal raw material have shown potential: (a) calcium silicate brick, (b) aerated concrete, and (c) poured concrete. In general, production of autoclaved products from scrubber sludges is technically sound, but lacks economic sureness. The calcium-silicate bricks have the advantage of binding the sulfur components within a calcium-silicate matrix. They are immediately marketable. In addition, the compressive breaking strengths of these bricks

are 3,500,000 kg/m² (5,000 psi) as compared to the minimum ASTM specification of 3,200,000 kg/m² (4,500 psi). The envisioned utilization areas for these brick are low-cost construction materials, decorative and interior walls, and acoustic insulating walls.

Aerated concrete is used commonly as a structural material in Europe. The product has a density of $0.8\text{-}0.9~\text{g/m}^3$ (50-56 lb/ft³) and a controllable compressive strength between 280,000 - $600,000~\text{kg/m}^2$ (400-850 psi). Envisioned areas of utilization are in non-load bearing walls, interior surfacing for exterior walls and sandwich construction with brick or concrete for insulating purposes.

The feasibility of using scrubber sludge as the cementing agent for the production of concrete block was also studied (CO-118). The product has a bulk density of 1.4 g/cm³ (90 lbs/ft³) and a compressive strength of ca. $630,000 \text{ kg/m}^2$ (900 psi) as compared to 2.4 g/cm³ (150 lbs/ft³) and 700,000 kg/m² (1000 psi) for conventional block.

Mineral Wool

The technology for producing mineral wool from fly ash has been developed by the Coal Research Bureau at West Virginia. The physical characteristics of wool fibers produced from scrubber sludge are reported to equal or excel commercially available mineral wool (CO-118). It is expected that mineral wool will find use as insulation material in electrical testing. Although technically feasible, this approach is not considered economically attractive because of its inability to compete with conventional mineral wool (AE-003).

Soil Amendment and Soil Stabilization

Several Virginia and West Virginia research groups have cooperated to study the properties of scrubber sludge with respect to soil amendment and soil stabilization (WE-074). The concensus is that as a result of the low cost of modified ash and its forecast abundance, the neutralizing powers and soil stabilization abilities of this desulfurization sludge can be put to use in reclamation of strip mines, spoil banks and other highly acidic áreas which texturally cannot sustain or support plant growth. Modified fly ash can be employed in agriculture to regulate the pH of the soil as well as the boron supplying power of certain soils. An additional advantage is that dewatering may not be necessary for direct application of the ash, although this is not certain at this time. Possible adverse effects due to excessive buildup of elements such as boron and molybdenum require further investigation.

To summarize the potential for sludge utilization, it appears that several possible markets for scrubber sludge could develop. It is likely, however, that the growth of these markets will lag far behind the growth of sludge production, resulting in the great majority of sludge being disposed of as a throwaway product. The circumstances at some plants might be such that most or all of their sludge could be marketed, however.

4.0 PRESENT AND PLANNED UTILITY INDUSTRY DISPOSAL PROGRAMS

Those utilities currently operating lime or limestone scrubbing systems are faced with the immediate problem of disposal of waste sludges. Other utilities committed to a sludge generating system for future installation are in a similar position. There is little experience in dealing with this waste material on a large scale, and what data and results have been obtained are not always released. The purpose of this section of the report is to review current and planned practices regarding disposal of scrubber sludges on an industrial level. The results of an EPA survey of utilities regarding sludge treatment techniques are summarized in Table 6.

Ponding is currently being employed by a number of utilities including the following:

TVA- Shawnee

NSP - Black Dog

SCE - Mohave

KP&L - Lawrence

KCP&L - Hawthorne

KCP&L - LaCygne

TVA's Widow Creek installation will include ponding facilities for both sludge and ash disposal. In addition, Lousiville Gas and Electric (Paddy's Run) and City of Key West (Stock Island) are presently disposing of their scrubber sludges by unfixed landfill; Montana Power Company is considering dumping their untreated sulfur oxide sludges in an abandoned strip mine area. In essence, these are also ponding operations. A solar evaporation pond is planned for Arizona Public Service's Cholla facility.

TABLE 6 POTENTIAL SLUDGE TREATMENT/DISPOSAL PROGRAM UTILITY PARTICIPANTS (JO-083)

(X = Current; P = Possible Additions)

Facility	Sorbent	T	<u> </u>	Dewater	ing Techni	Final Disposition				
(Availability	Fuel		Clari-		Centri-	1				1
Status)		Scale	fier	Filter	fuge	Dryer	Pond	Ponding	Landfill	Other
TVA-Shawnee (Current)	Limestone now, lime later	Proto- type	х	х	X			x		
	Eastern coal							(unlined)	•	
City of Key West-Stock Island (Current)	Limestone (coral marl) Residual oil	Full					х		X (Unfixed)	
Commonwealth Edison CoWill County (Current)	Limestone Eastern coal	Full	х	P		Р	X (Well points)		X (Sealed) (Fixed)	
Southern California Edison-Mohave	Limestone & lime Western coal	Pilot	х	х	Х			x		
Kansas City Power & Light- Hawthorn (Current)	Boiler injected limestone Coal (possible E&W blend)	Full	х				X (Well points)	X (unlined)		
Kansas Power & Light- Lawrence (Current)	Boiler injected limestone Eastern coal	Ful1		·			х	X (unlined)		
Louisville Gas & Electric- Paddy's Run (Current)	Carbide sludge (Ca(OH) ₂) Eastern coal	Full	х	х					x	

ò

TABLE 6 (Cont.)

POTENTIAL SLUDGE TREATMENT/DISPOSAL PROGRAM UTILITY PARTICIPANTS (JO-083)

(X = Current; P = Possible Additions)

	Facility	Sorbent		<u> </u>	I	Dewat	ering Tec	Final Disposition				
	(Availability Status)		53	6-1-	Clari-	5 .1.	Centri-		2-1	2		0.1
-84-	Northern States Power- Black Dog (Current)	Limestone	Western coal	Scale Pilot	fier X	Filter	fuge	Dryer	Pond	Ponding X (unlined)	Landfill	Other
	Kansas City Power & Light- LaCygne (Current)	Limestone	Eastern coal	Full						X (unl i ned)		
	Arizona Public Service- Cholla (Approx mid-1973)	Limestone	Western	Full						X (Solar evap) (unlined)		
	Duquesne Light- Phillips (Approx mid-1973)	Lime	Eastern coal	Full	Х				X (Curing)		X (Fixed)	
	Detroit Edison- St. Clair (Late 1973)	Limestone	Eastern coal	Full					х		X (Unfixed)	
-	TVA- Widows Creek (1975)	Limestone	Eastern coal	Ful1					х	X (unlined)		

The only utility presently employing a fixation process to produce a stabilized landfill material is Commonwealth Edison at Will County. Several utilities including Duquesne Light are now testing one or more fixation techniques for future use in landfill operations.

EPA's prototype scrubbing facility at Shawnee is currently testing both lime and limestone. The facility is being used to test several modes of sludge treatment, all entailing ponding as an ultimate disposal approach. The three configurations are:

- clarifier/pond
- clarifier/solid bowl centrifuge/pond
- clarifier/rotary vacuum filter/pond

Bench scale studies of the various dewatering techniques (described in Section 3.1.2.1) were used as the basis for selection of sludge treatment options. Another aspect being investigated in TVA's labs is the ability of settled sludge to seal clay linings. Sludge from this facility has been sampled and analyzed by Aerospace Corporation under contract to EPA in an attempt to characterize scrubber sludges and define any potential problems which may be incurred in its disposal. Results of this investigation have been presented throughout this report.

The pond itself is divided into three sections. The dikes are made from fly ash and covered with a local clay. A monitoring program was installed around the pond to observe seepage, which was reported to be fairly heavy during initial operation of the pond before any solids had settled. Under closed loop

operation, sludge is discharged to a large settling area from the scrubber circuit, thickener underflow, and/or filter or centrifuge. The supernatant is returned via a small "polishing" pond.

Two clarifiers were evaluated, one 6.1 meter in diameter and a larger one 9.1 meter in diameter. The smaller of the two proved to have been underdesigned. This was a direct result of the poor settling characteristics observed. The concentration of the underflow approached 40% solids which was the final expected settled composition. The following recommendations were made concerning optimum sludge handling:

- · maintain steady feed flow to clarifier
- optimize sulfite oxidation
- investigate effect of limestone particle size on settling characteristics
- control density of clarifier underflow let level of sludge vary
- operate clarifier in series with filter or centrifuge
- · use flocculants

At Widows Creek a new pond for disposal of sludge generated by the limestone scrubber is under construction which will have an initial seven year capacity of $3.4~\mathrm{MM}~\mathrm{m}^3$ ($4.5~\mathrm{MM}~\mathrm{yd}^3$) (MC-068, TE-113, SL-034). This can be increased by $1.0~\mathrm{MM}~\mathrm{m}^3$

(1.3 MM yd³) by raising the dikes. An estimated additional 2.7 MM m³ (3.5 MM yd³) of capacity for which no provision has yet been made may be needed before 1995. A total of 0.93 km² (230 acres) of land is taken up by the new pond which is sectioned for separate disposal of ash and sludge. The pond is unlined; the perimeter and divider dikes are 9.1 meters (30 feet) tall with 1.2 meters (4 feet) of freeboard and constructed of compacted earth.

Under closed loop operation, the scrubber wastes will be pumped to the sludge disposal section of the pond as a 15-16% solids slurry. The ash pond effluent will be released to the Guntersville Reservoir. A thickener will not be employed. A final settled density of 40% solids is expected, based on pilot plant data showing 57-66% water content after 240 days of settling. The overall disposal rate is calculated to be $115 \, \mathrm{m}^3/\mathrm{hr}$ (150 yd $^3/\mathrm{hr}$).

Northern States Power is currently employing ponding operations to dispose of the sludge and ash from the pilot scale limestone scrubber at Black Dog Station (J0-083). Clarification is used for primary sludge dewatering. A future limestone scrubber installation is planned for NSP's Sherburne County site. There sealed basins will receive the clarified solids, with clarifier liquor being recycled (SW-011). The precipitated solids and unreacted limestone will be carried to the pond by wash water where they will be disposed of together with fly ash. Supernatant from the pond will also be recycled (J0-090).

The pilot scrubber at Southern California Edison's Mohave Station will be tested under both limestone and lime scrubbing conditions. Three modes of sludge separation are under investigation: centrifugation, rotary filtration, and

clarification (WE-068); the effect of degree of oxidation of sulfite is also being studied. No results of these tests were presented. Ponding is being utilized as the final disposal method.

The full scale boiler injected limestone scrubbers, Units 4 and 5 at Kansas Power and Light's Lawrence Station, operate under closed loop. Ponding is used both as a dewatering technique and an ultimate disposal approach. An experimental sludge pond has been constructed; fourteen well points have been placed outside the perimeter (TA-040). A monitoring study is being carried out in conjunction with Combustion Engineering to determine possible adverse effects on the groundwater. Samples of groundwater will be taken weekly for two months prior to introduction of sludge to the pond and will continue for one year thereafter. Preliminary results are not available for release at this time.

Kansas City Power and Light is currently running two full scale limestone systems at LaCygne and Hawthorn Stations. At the Hawthorn site clarification and ponding are employed to dewater the sludge. Ultimate disposal is by ponding at both locations (JO-083).

The current and future sludge disposal practices for Paddy's Run, Louisville Gas and Electric, involve landfill operations. The scrubber itself is a full scale carbide sludge $\lceil \text{Ca}(\text{OH})_{\text{p}} \rceil$ system. Clarification and vacuum filtration result in a 50% solids sludge which is temporarily placed in an interim pond. At the present time, the sludge is being trucked to an off-site disposal area, a trench excavated by the Kentucky Highway Department. The sludge receives no stabilization treatment. Future plans, however, may include such treatment; the

utility is currently looking at those offered by Dravo and IUCS. Research in this area is also being conducted by the University of Kentucky and the State Highway Department. Another aspect of sludge disposal being considered by the utility is pipelining the solid waste slurry to the fixation site (VA-068).

Experience in untreated sludge disposal has also been obtained at the City of Key West's Stock Island facility where a prototype (37 MW) limestone process has been operating. Residual oil is burned, thus resulting in a solid waste of low ash content. The scrubber solids are placed in one of two settling ponds where drying takes place (PA-049). While one pond is being filled, the other is emptied. The dried sludge is then dumped in an adjacent 81,000 m² (20 acre) city owned site which is bay bottom land. The material has been placed above sea level in compliance with a Florida state law which prohibits filling of submerged land productive to marine life.

The approach under consideration by the Montana Power Company entails disposal of their desulfurization sludges in abandoned strip mine areas. Coal ash high in CaO and MgO is to be used as an absorbent material.

Because of the climatic conditions at Arizona Public Service's Cholla facility, a solar evaporation pond will be used as a sludge disposal technique. The clarifier underflow from the 115 MW limestone system will be transported to the existing ash pond (MU-022). Clarifier effluent will be recycled under the closed loop operation.

Commonwealth Edison has the greatest amount of industrial experience with disposal of stabilized sulfur oxide sludges. The full scale limestone scrubber is installed on Will

County's Unit 1 boiler (163 MW). Initially, a 22,000 m² (5.5 acre) pond 1.8 meters (6 feet) deep was used for sludge disposal, but since it has a limited (6 months) capacity, another approach was sought. Presently, the spent slurry from the scrubber is pumped to a clarifier 20 meters (65 feet) in diameter. The underflow is temporarily held in a pond where further dewatering occurs. The pond supernatant and the clarifier liquor are returned to the scrubber cycle via a second pond. watered sludge is pumped to a loading station where it is mixed in a cement truck with fly ash and other dry ingredients to produce a stable landfill material. Chicago Fly Ash is under contract to carry out the stabilization and disposal operations (ST-117). The fixed material is presently being placed in an on-site clay lined basin approximately half a mile away. practice will continue until the environmental soundness of the material has been demonstrated (GI-017). In the future, they plan to utilize additional dewatering procedures such as vacuum filtration and possibly thermal disc dryers to reduce the volume of sludge requiring stabilization treatment.

Pilot scale sludge samples generated by the lime scrubbing system at Duquesne Light's Phillips Station have been tested and characterized by Dravo Corporation. When the full scale system starts up, the sludge disposal method will entail a fixed landfill operation in conjunction with clarification and curing pond as dewatering methods. Dravo Corporation, which has been working on dewatering and stabilizing Duquesne's sludges on a bench scale up to now, is being considered to provide the industrial scale disposal process.

For a detailed description of the project underway at STEAG, see Appendix B. There an experimental sludge pond is being monitored to determine extent of potential groundwater contamination.

Two dual stage venturi scrubbing systems utilizing carbide sludge as an absorbent have been retrofitted to the 156 MW power plant of the Mitsui Aluminum Company. The unit has operated under continuous closed loop mode since March, 1972, with no significant scaling or plugging problems. A bleed stream from the system containing mostly calcium sulfite (80%) and calcium sulfate is disposed of in a preexisting 90,000 square meters ash pond (SA-099). Pond liquor which is saturated with respect to calcium sulfate is recycled via rubber lined piping to the scrubber circuit for reuse. Now that this SO₂ control system has begun operation, production of high quality gypsum from waste sludge is planned. There is a definite market for by-product gypsum in Japan for the very near future. However, the Japanese supply of this by-product is soon expected to exceed the demand (AN-059).

5.0 <u>CONCLUSIONS</u>

Lime and limestone scrubbing systems will have wide application for SO_2 removal in the next decade. Since removal of one pound of sulfur will generate approximately ten pounds of wet sludge, a tremendous amount of solid wastes will be generated. Because of the large quantities involved, the environmental effects of disposal of this material is a matter of considerable concern. A quantification of these effects and the identification of environmentally acceptable disposal techniques are, therefore, of great importance.

A limited amount of data is available on the chemical nature of various sludge materials, and this data can be used to help quantify potential environmental effects of sludge disposal. Sludges from different units exhibit a wide variation in chemical properties. Since there are no large scale units with a lengthy history of continuous operation, it is not clear how applicable existing data are to such a system. Nevertheless, those data have been used to put the problem into perspective (see Section 2.1). The main problem area related to sludge disposal appears to be the presence of soluble materials in the sludge, resulting in potential water pollution problems for both surface and groundwater. The soluble species can be classified as follows:

- (1) Soluble toxic species, e.g., trace metals
- (2) Excessive total dissolved solids
- (3) Excessive levels of specific species not generally thought of as toxic, e.g., sulfate and chloride

A consequence of the presence of soluble species is that careful attention must be paid to the design and operation of sludge disposal sites. It appears that many variables (coal, limestone, and operating parameters) can influence the amount of the soluble species. More work is needed to quantify the extent of influence of these variables on sludge composition and behavior, and to better define the chemical characteristics of sludge from large continuously operating systems. Several studies are under way at power generating stations around the country which may provide some of this type of information. EPA is also funding efforts in this area.

A limited amount of data are also available regarding the physical properties of sludge (Section 2.2). Again, there is a wide variation in properties for sludges from different These properties are influenced by many system variables in a manner that is not well understood. The physical properties strongly influence the ease with which the material may be handled and transported, and magnitude of the land reclamation problems for abandoned sludge disposal sites. The main problems with regard to the physical properties of sludge are difficulty in dewatering and a tendency to rewater to its original water content and permeability. A lack of strength by dried unfixed sludge material is another potential problem. In terms of handling problems, special dewatering techniques (besides settling) may be required. In terms of land reclamation, the effects of rewatering and lack of load bearing strength have not been quantified. Another land reclamation problem which has not been addressed is the ability of the sludge to support growth of vegetation.

Electric utilities who now operate or plan to install lime/limestone scrubbing systems in the State of Ohio are faced

with selecting at least an interim sludge disposal scheme. On the basis of the information contained in this report, the following should be taken into consideration determining the method to be employed:

- Ponding and landfill are the most viable alternatives.
- Stabilized landfill offers a more permanent solution.
- Geography will determine disposal site and technique in many situations.
- Utilization may be feasible in special cases although the probability is extremely low, especially in the near future.

The major disposal options for sludge are ponding and landfilling. Even though the presently available data on chemical and physical properties indicate some potential problem areas, it appears that both of these disposal options are viable methods if proper engineering and operation are practiced.

Ponding of sludges, which probably will account for 60% of sludge disposal based on existing and planned installations, will require particular attention to proper practice because of the increased potential for groundwater pollution (see Section 3.1.1.2). This type of pollution is particularly bad because, unlike surface water pollution, there is little opportunity for dilution of the contaminants, and the pollution may go undetected. With proper site selection and pond lining, however, leaching of contaminants to an aquifer from a pond can be avoided. It

appears that overflow of pond liquor into surface water should and can be avoided. This will require proper pond design and partial or total recycle of pond liquor, with treatment of any blowdown streams. The construction and lining of ponds is established technology.

Landfilling (Section 3.1.2) probably will account for some 40% of the sludge disposal, based on existing and planned projects (this percentage may increase as the state of the art of fixation advances and costs decrease). Whereas ponding is largely planned with untreated sludge, the physical properties of sludge may necessitate treatment (fixation) by one of several commercially available processes to convert the sludge to a more easily handled The feasibility of landfilling without fixation requires further investigation at this point. Even if the sludge is not treated, some type of dewatering will likely be required. An additional advantage claimed for sludge fixation is a great decrease in the permeability and amount of soluble species in the sludge. Since landfilling basically presents the same type of potential water pollution problems as ponding, fixation might eliminate the need for such procedures as linings and cover material for disposal sites. Both dewatering and fixation processes are currently being tested and compared by several independent groups in order to determine the technical feasibility of each. Results available to date seem to indicate that stabilized landfill may provide the most permanent solution to the disposal of throwaway products from SO, removal systems. Reliable economic data associated with this disposal scheme, however, are not available at this time because of the lack of long term, full scale applications in this area.

Another consideration in the selection of a disposal site is the geography and hydrogeology of the area. This will be unique to each Ohio utility. These factors will influence

the economic and the environmental aspects of the disposal method in the event that contamination of groundwaters by sludge is shown to be a problem. Precautionary measures such as liners, covers, fixation or drainage facilities will be selected, if needed, on the basis of the geology. For instance, if the water table is in close proximity to the bottom of the disposal site (pond or landfill), or if the soil is extremely permeable to potential leachate, then preventive measures will be required.

Commercial utilization of scrubber sludges at this stage of development appears unfeasible to any great extent. The variability in the sludge composition and properties (amount of ash, water content, calcium sulfite and sulfate concentrations, water retention, etc.) is one hinderance to extensive utilization. A second obstacle is the sheer volumes forecast on a nationwide basis (see Section 1.0). It has been shown that several of the utilization schemes may be technically promising. However, it is unlikely that any great percentage of sludge generated could be utilized in any one commercial market.

In conclusion, based on presently available data, there are no insurmountable technological problems in disposing of sludge in an environmentally acceptable manner. The economics of such disposal have not been well defined, but the results of numerous studies now under way at pilot plants and full scale systems around the country will soon provide additional information in this area, as well as providing improved data on the chemical and physical properties of untreated and treated (fixed) sludge and its permeability and leachability.

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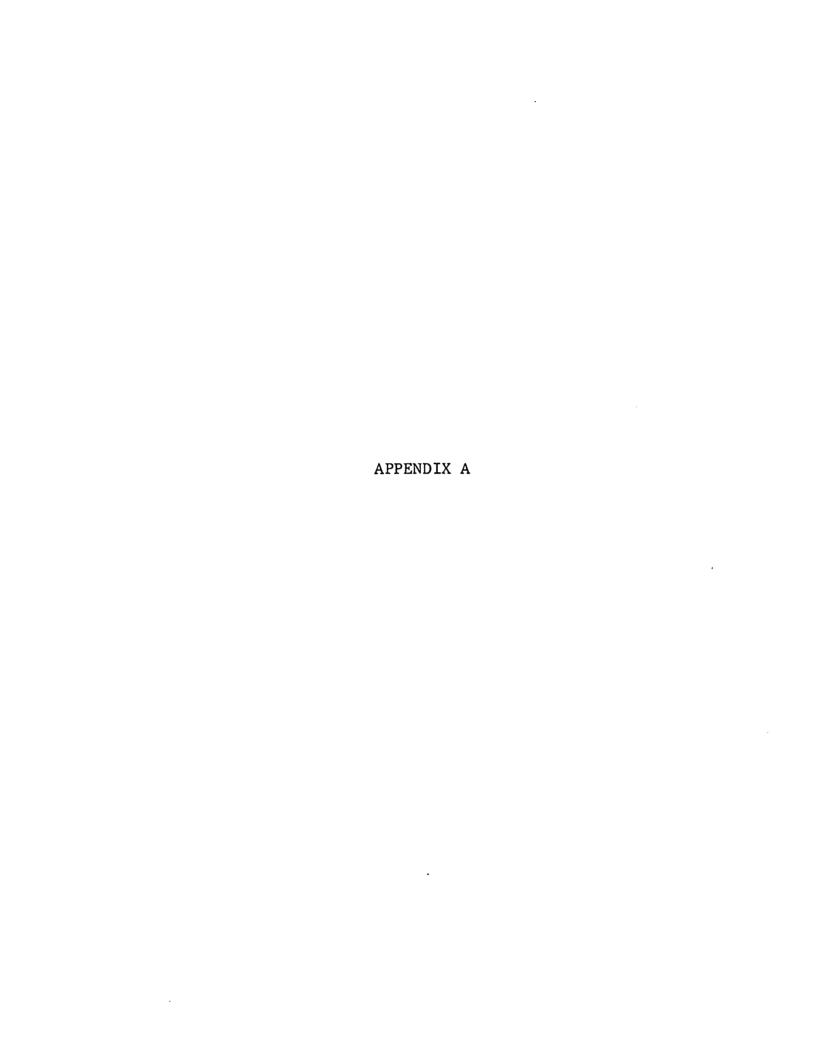


TABLE A1

ELEMENTAL COMPOSITIONS OF COAL AND ASH (IN ppm)

	l Eastern Coal (Shawnee)	2 Western Coal (Composite)	3 Bottom Ash (Western Coal)	4 Bottom Ash (Eastern Coal Shawnee)	5 Fly Ash (Eastern Coal Shawnee)	6 Fly Ash (Eastern Coal Shawnee)	7 Fly Ash (Western Coal)
Analytical Method	Spark Source Mass Spectro- graphic Analysis	Not Reported	Not Reported	Siark Source Mass Spectro- graphic Analysis	Spark Source Mass Spectro- graphic Analysis	Spark Source Mass Spectro- graphic Analysis	Not Reported
Ref.	AE-008, RO-084	RO-084	RO-084	AE-008	AE-008	AE-008	RO-084
Li	3.3			42	(Scrubber Inlet) 6.5	(Scrubber Outlet)	
Na	1700			350	870	2800	
K	3000			1300	960	2500	
Rb	24			63	11	40	
Cs	N.D.			6.0	1.3	1.4	
Be	<0.01	N.D.	<2				3
Mg	1700			9700	4400	5700	
Sr	1100	••		170	400	1300	
Ва	1800	400	1500	(<1%)	1000	6400	5000
В	46	15	70	220	38	220	300
A1	7500		••	(<1%)			
С	(>1%)			2500	2000	7000	
Pb	30	4	20	N.D.	27	64	30
N	30			3	5.1	230	
P	40			680	140	1800	
As	N.D.	3	3	3	22	450	15
Sb	<0.05	0.17	0.26				2.1
s	(>1%)			200	440	1200	
Se	N.D.	1.6	1				18
F	7.9		••	4.1	4.2	30	
C1	280	38		17	25	58	••
Br	N.D.		••	N.D.	6.5	N.D.	₩.₩

TABLE Al Continued
ELEMENTAL COMPOSITIONS OF COAL AND ASH (IN ppm)

	1 Eastern Coal (Shawnee)	2 Western Coal (Composite)	3 Bottom Ash (Western Coal)	4 Bottom Ash (Eastern Coal Shawnee)	5 Fly Ash (Eastern Coal Shawnee)	6 Fly Ash (Eastern Coal Shawnee)	7 Fly Ash (Western Coal)
Ti	5900			(>1%)	6000	(>1%)	
v	180	9	70	290	65	820	150
Cr	310	5	70	700	440	230	150
Mn	350	15	150	530	180	290	150
Fe	4500			(>1%)			
Ni	N.D.	25	15				70
Cu	N.D.		** **	220	25	140	
Zn	180	0.56	25	640	290	1600	70
Y	95			340	73	47	
Cd	N.D.	<0.5	<0.5				<0.5
Hg	<0.01	0.05	<0.01				0.03

TABLE A2
CHEMICAL COMPOSITION OF FLY ASH - MAJOR AND MINOR CONSTITUENTS

	National Range for Typical Samples	Bituminous	Lignite
Na _e O	0.4 - 1.5	0.05	0.87
K ₂ O	· 	1.42	0.68
MgO	0.5 - 1.1	1.00	7.31
Ca0	1.5 - 4.7	4.48	18.00
В	0.1 - 0.6		
$A1_a0_3$	20 - 30	16.25	10.70
С	0.1 - 4.0	2.21	0.11
SiO ₂	30 - 50	49.10	32.60
P	0.01 - 0.03		
SO ₃	0.02 - 3.2	0.73	2.60
TiO2	0.4 - 1.3	1.09	0.56
Fe ₂ O ₃	10 - 30	22.31	10.00
Ref.	RO-093	CO-119	CO-119

TABLE A3

CHEMICAL COMPOSITION OF ASH PONDS

		Solids (wt %)				Liquors (ppm)				
	Oak Ridge Y-12 Stea A ¹ B ²		Oak Ridge Y-12 Steam Plant B C Unidentified Ash Pond (EPA Data)		Ash Pond	Range for Ten Ohio Plants	TVA's Widow Creek Ash Pond 1971 Quarterly Samples			
							1/4	4/5	7/6	10/4
	Analytical Method	Spectrograp	hic Spectrograp	hic Spectrographic		**				
	Ref.	SC-122	SC-122	SC-122	RO-084	RO-093	TE-112	TE-112	TE-112	TE-112
	pН				~~	6.2-11.5	7.3	9.0	9.8	9.1
	Li	0.04	0.08	0.08						•
	Na	0.6	0.7	0.6						
	K		3	2.5						
A-4	_				0.000					
4	Бе				0.002					
•	Mg	0.6	1.0	0.9			4.6	3.4	3.7	4.3
	Ca	0.6	0.6	0.6			20	34	47	45
	Ва	0.12	0.12	0.10	0.07					
	В	0.03	0.05	0.05	0.5	<100-1600				
	A1	>20	20	18						
	С	12.08	11.94	12.51						
	Si	20	35	30		as SiO _g	{ 5.4	4.4	6.1	5.6
	РЬ	0.01	<0.01	<0.01	0.01		٠			
	N					$\begin{cases} 0.1 - 1.9 \text{ (as} \\ \sim 0.1 \text{ (as NO}_x \text{)} \end{cases}$				
	P					0.1 - 0.6				
	As				0.01					• •
	Sb				0.015					

A-4

TABLE A3 Continued
CHEMICAL COMPOSITION OF ASH PONDS

Solids (wt %) Liquors (ppm) Range for Ten Ohio Plants Oak Ridge Y-12 Steam Plant Unidentified TVA's Widow Creek Ash Pond Ash Pond 1971 (EPA Data) Quarterly Samples 7/6 1/4 4/5 10/4 --100 95 S(as SO₄) 70 60 --Se 0.035 --21 11 19 C1 17 Τi 0.3 1.0 0.8 0.03 0.04 0.08 0.03 0.03 0.03 Cr 0.075 0.44 0.02 <0.01 0.04 0.04 0.08 0.02 Mn 7 Fe 10 10 0.29 0.42 0.27 0.69 0.02 0.03 0.03 0.015 Ni 0.03 0.02 0.03 Cu 0.03 Zn Cd 0.01 <0.001 Hg Total Dissolved 240 190 210 210 Solids

¹ Sample A was collected at the overflow from the primary retention basin to a water-filled quarry which acts as a settling pond.

² Sample B was collected at the outfall of the quarry.

³ Sample C was collected where the overflow enters a lagoon of a lake.

TABLE A4

CHEMICAL ANALYSES OF LIMESTONE (WT. %)

Sample	Shawnee Limestone	Shawnee Limestone	Western Limestone	Western Limestone
Analytical Method	Emission Spectrographic Analysis	Spark Source Mass Spectro- graphic Analysis	Emission Spectrographic Analysis	Spark Source Mass Spectro- graphic Analysis
Ref.	AE-007	AE-008	AE-009	AE-009
Li		0.00018		0.000031
Na	0.036	0.0360	TR<0.06	0.17
K	ND	0.0580	ND<0.40	0.033
Rb		0.00017		0.00007
Cs		ND		ND
Mg	2.9	>1	0.30	0.40
Ca	35.		39.	
Sr	0.078	0.15	0.039	0.0220
Ва		0.0010	ND<0.20	ND
В	ND	0.00015	ND<0.005	0.000080
Al	0.012	0.42	0.0099	0.33
Ga	ND		ND<0.006	
С		0.4900		
Si	0.65		0.24	
Sn			ND<0.008	
Pb	ND	ND	ND<0.01	
N		0.00045		0.00022
P		0.0085	ND<0.50	0.0050
As		ND	••	0.0011
s		0.9220		0.0030

Balance is sulfate, sulfite, oxides, and carbonates

TABLE A4 Continued
Chemical Analyses of Limestone (Wt. %)

Sample	Shawnee Limestone ¹	Shawnee Limestone [:]	Western Limestone ¹	Western Limestone ¹
Analytical Method	Emission Spectrographic Analysis	Spark Source Mass Spectro- graphic Analysis	Emission Spectrographic Analysis	Spark Source Mass Spectro- graphic Analysis
F		0.0012	••	0.00043
C1		.0038		
Br		ND	••	-~
Ti	ND	0.0440	ND<0.004	0.0160
v	••	0.0015	ND<0.008	0.00053
Cr	0.00084	0.00076	0.0014	0.0019
Mn	0.011	0.0140	0.025	0.0150
Fe	0.10	0.25	0.070	0.0900
Co	ND		ND<0.002	
Ni	ND		ND<0.002	
Cư	0.00011	ND	0.00022	ND
Zn		0.0059	ND<0.06	
Y		ND		0.006
Мо	Nil			

Balance is sulfate, sulfite, oxides and carbonates

TABLE A5

WET CHEMICAL ANALYSIS OF SLUDGE STANDARDS (WT. %)*

	STD II	STD III	STD IV	STD V	STD VI	STD VIA	STD VII	STD VIII	STD IX
SiO ₂	1.5	30.7	0.79	19.4	1.1	27.7	4.6	1.2	2.0
Al_2O_3	0.32	6.6	0.05	6.8	0.01	14.7	2.3	0.48	0.45
Fe ₂ 0 ₃	0.27	8.6	0.18	5.4	0.09	8.3	1.6	0.72	0.72
Ca0	49.6	22.7	42.5	27.6	52.5	24.2	40.1	42.5	46.2
MgO	0.54	1.5	0.10	3.2	0.52	0.70	0.20	0.90	0.40
NagO	0.04	0.50	0.03	0.08	0.02	0.16	0.05	0.05	0.04
K ₂ O	0.17	1.1	0.05	0.24	0.14	1.2	0.29	0.07	0.21
TiO ₂	<0.02	0.26	<0.02	0.32	<0.02	0.79	0.11	<0.02	<0.02
P_2O_5	0.05	0.11	0.06	0.08	0.13	0.19	0.08	0.06	0.07
CO³	29.2	5.3	3.7	7.2	36.6	15.3	13.6	11.5	24.4
SO ₂	11.7	5.8	38.8	2.2	6.3	3.4	5.4	24.1	13.7
SO ₃	3.5	6.5	3.3	12.3	0.5	<0.1	24.9	8.4	4.4
CaCO ₃	65.7	12.0	8.4	16.3	80.6	34.7	30.9	26.1	55.4

From TA-040

IDENTIFICATION OF SLUDGE STANDARDS

STD II - C-E sludge - CaCO₃, 150% stoichiometry, 2000 ppm SO₂

STD III - Kansas Power and Light sludge

STD IV - C-E sludge - Ca(OH)₂, 38% to 50% stoichiometry, 50 to 60% SO₂ removal, slurry feed 220 gpm, recycle 165 gpm with 55 gpm blowdown

STD V - Union Electric sludge

STD VI - C-E sludge - CaCO₃, 150% stoichiometry, 45 to 55% removal, no recycle

STD VIA - STD VI plus 50% STD I (fly ash)

STD VII - C-E sludge - 300 to 325% stoichiometry, 64% SO₂ removal, 300 lb/hr fly ash, 550 lb/hr CaCO₃

STD VIII - C-E sludge - 120 to 130% stoichiometry Ca(OH), 90.8% removal, 120 gpm (Ca(OH), slurry underbed, inlet SO, 860 to 840 ppm, outlet SO, 80 ppm, 145 lb/hr Ca(OH), no fly ash addition

STD IX - C-E sludge - 220 gpm H₂0 spray, 275 lb/hr lime feed, 300 F reaction temperature

TABLE A6

SPARK SOURCE MASS SPECTROGRAPHIC ANALYSIS OF SCRUBBER SOLIDS*

(In Parts Per Million By Weight)

	1	2	3
	TCA Effluent		
F1	Separated	TCA Effluent	Clarifier
Element	Solids	Slurry Solids	Solids
Li	5.1	7.9	1.2
В	28	42	7.6
С	1,700	170	140
N	1	3	3
F	30	16	5.9
Na	2,800	290	270
Mg	(>1%)	(>1%)	(>1%)
A1	(>1%)	(>1%)	(>1%)
P	170	150	110
S	(>1%)	2,100	330
C1	47	79	42
ĸ	3,700	760	860
Ti	4,500	5,300	4,200
v	94	150	150
v Cr	240	250	66
OI.	240	250	00
Mn	180	230	190
Fe	(>1%)	(>1%)	(>1%)
Cu	33	49	N.D.
Zn	330	450	90
As	24	53	16
Rb	13	30	9.0
Sr	750	1,500	1,100
Y	63	45	27
Cs	1	1.2	N.D.
Ba	1,600	870	520
		<i>C.L.</i>	N D
Pb	20	64	N.D.
Br	N.D.	N.D.	N.D.

Notes:

- 1. Sample for columns 1, 2, and 3 were centrifuged and dried at Aerospace.
- 2. Samples for colums 1 and 2 were obtained upstream of the clarifier. Column 1 sample was filtered at the scrubber site.
- * From AE-008

TABLE A7 EMISSION SPECTROGRAPHIC ANALYSES OF LIMESTONE AND CLARIFIER LIQUOR AND SOLID*

	Distilled Water ppm	Clarifier Liquor ppm	Clarifier Solids Wt. %
Ca	TR < 0.004	1100.	27.
Mg	0.0040	67.	1.4
Si	0.085	14.	8.9
В	0.018	11.	0.0092
Mn	**ND < 0.01	1.6	0.013
Fe	0.055	0.17	0.25
A1	ND < 0.04	0.34	2.6
Мо	< 0.02	0.56	Nil
Çu	0.0064	0.0017	0.00053
Na	ND < 1.0	***TR < 7.5	0.23
Ni	0.058	0.05	0.0017
Sr	ND < 0.01	2.1	0.099
K	ND < 2.0	19.	0.88
Со	Nil	Nil	TR < 0.001
Cr	Nil	Nil	0.0025
Ti	Nil	Nil	0.53
Pb	Nil	Nil	0.015
Ca	Ni1	Nil	0.0027
Other Cations	Nil	Nil	Nil

Balance is sulfate, sulfite, oxides and carbonates
"From AE-007
**ND - Not detected
***TR - Trace



EMISSION SPECTROGRAPHIC ANALYSIS OF SOLIDS FROM A WESTERN STATION*

Element	Scrubber Input From Holding Tank	Scrubber Output To Holding Tank	Centrifuged Solids	Centrate		ke-Up ater
Si	10.%	1.6%	1.4%	18.%	•	22.%
Ca	25.	35.	37.	4.2		9.6
Fe	1.2	0.29	0.18	3.6		4.2
Al	3.4	0.90	0.79	15.		6.2
Mg	0.53	0.18	0.20	1.3	•	1.4
Na	2.4	1.6	0.69	5.2	TR <	0.20
Ba	ND < 0.20	<i></i>		0.19	TR <	0.20
В	TR < 0.005	0.0063	TR < 0.005	0.016		0.017
P	ND < 0.50			TR < 0.50		2.6
Ti	0.10	0.056	0.044	0.94		0.12
Mn	0.017	0.0076	• 0.0055	0.046		0.13
K	TR < 0.40	TR < 0.40		0.94	ND <	0.40
Рb	TR < 0.02	0.016	TR < 0.01	0.064		0.034
Ga	ND < 0.006			0.024	TR >	0.006
Cr	0.0071	0.0070	0.0042	0.072		0.038
Ms	ND < 0.004			0.0088	ND >	0.004
Sn	ND < 0.008				TR >	0.008
v	ND < 0.008			0.030	ND >	0.008
Cu	0.0041	0.0025	0.00089	0.036		0.38
Zn	ND < 0.06					0.86
Ni	0.0024	0.0041	0.0029	0.014		0.0028
Co	ND < 0.002			0.0043	TR <	0.002
Sr	0.030	0.11	0.14	0.095		0.16
Other	Nil					

^{*}From AE-009

SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF SOLIDS
FROM A WESTERN STATION*

Element	Detection Limit, ppm	Scrubber Output to Holding Tank, ppm	Centrifuged Solids, ppm
Li	0.07	7.9	5.5
В	0.1	28	35
С	0.1	920	5,500
N	1	72	41
P	0.1	190	3,500
Na	0.07	(c)	(c)
Mg	0.7	7,400	5,600
A1	0.5	(c)	(c)
P	0.2	1,100	390
S	2	(c)	(c)
Cl	0.5	1,600	1,400
K	0.1	1,100	2,100
Ti	1	1,100	3,700
V	0.5	42	59
Cr	0.7	250	290
Mn	0.5	90	180
Fe	1	(c)	(c)
Cu	1	1	1
Zn	1	71	210
As	1	58	46
RЬ	0.7	22	7.3
Sr	3	1,700	1,600
Cs	3	53	N.D.
Ва	5	1,400	2,000

^{*}From AE-009

TABLE A10
(Private Communication)

	II	III	IV	V
Element or Constituent	Make-up Water	Scrubber Recycle Water	Scrubber Recycle Water After Lime Treatment	PHS Drinking Water Standards
В	-	64	33	-
Cd	.01	.07	.07	.01
Cu	.01	1.6	.02	1.
Pb	<.05	.4	.14	.05
Mg	44	236	-	-
Mn	.01	2.2	.16	.05
Нg	<.0002	.0002	-	-
Ni	<.05	2.2	.11	-
K	5.5	28	-	-
Na	780	2,080	. -	-
Zn	.01	2.3	.03	5.
Ag	-	.04	.02	.05
As	<.02	<.02	-	-
Ca	-	590	930	-
рН	9.6	3.3	9	-
Sulfates	310	9,000	3,700	250
TDS	2,500	15,400	-	500
Hardness as CaCO ₃	328	2,450	-	-

^{*}Ca(OH), treatment test to precipitate metallic elements; added Ca(OH), at or near stoichiometric; flocculated, settled, and filtered.

These data are from a pilot scrubber in which fly ash is used as an absorbent. The coal contains less than 1% sulfur, and a 40% reduction in SO_2 is achieved.

TABLE A11 (MO-028)

CONCENTRATIONS IN OPEN-AND CLOSED-SCRUBBER SYSTEMS

	Closed-Loop Mode Milligrams per Liter	Open-Loop Mode Milligrams per Liter
Calcium	1,600	1,100
Magnesium	1,150	*
Hardness (as CaCO ₃)	7,100	**2 ,700
Sulfite	5,400	1,700
Sulfate	6,500	2,600
Nitrate	1	6
Total Dissolved Solids	13,000	**7,000
рН	5.0	5.3

^{*}Not determined, MgO content of limestone less than 1%.
**Not determined, estimated minimum values.

These data are from a TVA pilot plant scrubber. The coal was 3% sulfur, the limestone had 1% MgO and was added at 150% of stoichiometric.

TABLE A12 (TE-113)

	Parameter Concentration (Closed Loop Operation)	Parameter Concentration (Open Loop Operation)
Calcium	(mg/1) 1058	(mg/1) 815
Magnesium	788	85
Hardness (as CaCO ₃	5890	2425
Sulfite	145	
Sulfate	3461	1450
Chlorides	1720	675
Sodium and Potassi Composite	Lum 105	59 ·
Total Dissolved So	olids 7277	4500

These data are from TVA's pilot plant at the Colbert Steam Plant. The sampling point was the effluent from the clarifier.

<u>TABLE A13</u> (TE-113)

		entrations, mg/ <i>l</i> c Wastes	Mist Eliminator	Alabama
	Open-Loop	Closed-Loop	Wash Water	Guidelines
Iron (Total)	0.17	0.07	0.11	3.0
Cyanide	< 0.01	< 0.01	< 0.01	< 0.1
Zinc	0.04	0.02	0.06	0.8
Nickel	0.22	< 0.05	0.25	0.5
Copper	0.035	0.03	0.04	0.5
Chromium (Total)	0.07	0.11	0.08	0.5
Chromium (Hexavalent)				0.1
Cadmium	0.004	< 0.001	0.0052	< 0.1
Phosphates (Total)	0.1	0.01	0.05	1.0

NOTE: These data are from TVA's pilot plant at the Colbert Steam Plant. The sampling point was the effluent from the clarifier.

TABLE A14 WET SIEVE ANALYSIS OF SCRUBBER SLUDGES (SE-066)

P. ...

	C	umulative	e Wt.% R€	etained	
	<u>+40M</u>	<u>+100M</u>	<u>+200M</u>	+325M (44µ)	+400M (37µ)
Fly Ash	0.2	1.7	7.1	15.1	
Eastern Coal Lime Sludge				7.5	13.5
Western Coal Lime Sludge					1.0
Dry/Wet Process Sludge					29.2
Limestone Sludge					18.4
Smelter Sludge					2.4

TABLE A15

SUB-SIEVE ANALYSIS OF FLY ASH AND AN

EASTERN COAL LIME SCRUBBER SLUDGE

(SE-066)

	Cumulative %								
	Fly Ash	Eastern Coal Sludge							
+50 Micron	15	1							
+40 Micron		2							
+30 Micron		5							
+20 Micron	27	12							
+17 Micron	32								
+15 Micron		21							
+10 Micron	47	39							
+ 7 Micron	62	51							
+ 5 Micron		68							
+ 2 Micron	92	88							
+ 1 Micron	97	·							
	A 17								

TABLE A16

Dravo Sample Identification

Eastern Coal Lime scrubbing sludge from a

power plant burning Eastern coal; ash present.

Lime scrubbing sludge from a power plant burning Western coal; no ash present. Western Coal

Dry Injected with Wet

4.

Scrubbing

Sludge produced by limestone

injected into the boiler followed by wet scrubbing;

ash present.

Limestone scrubbing sludge Limestone Scrubbing

from a pilot plant burning

oil; no ash.

Lime scrubbing sludge from Smelter Gas

molybdenum sulfide smelter;

no ash present.

TABLE A17
Blaine Indices for Untreated Scrubber Sludges

Sample (refer to Table Al6	Blaine Index (cm²/g)
Fly Ash	2,640
Eastern coal sludge	12,500
Western coal sludge	27,500
Dry injected/wet scrubber sludge	14,100
Limestone scrubbed sludge	11,100
Smelter sludge	3,670

TABLE A18
Settling Characteristics of Sludge

Sludge Source*	Wt % Solids
Eastern Coal	<30-45
Western Coal	21.5
Dry Injected with Wet Scrubbing	24
Limestone Scrubbing	39
Smelter Gas	37-40
Fly Ash	64

^{*} See Table A16 for sample identification.

TABLE A19

(from SE-066)

Centrifuge Tests - Pilot Plant Sludge Bird 6" Continuous Centrifuge 4130 RPM - 1400 G Force

Feed	Feed	Pool	Feed	Z	Effluent
	% Solids	Depth	Rate	Solids	Solids
		•	GPM *		%
Drum 8	33.6%	Intermediate	3.4	47.8	4.6%
Drum 8	33.6%	Minimum	3.4	48.1	0.9%
Drum 8	33.8%	Maximum	3.4	47.3	3.4%
Drum 8	29.8%	Maximum	3.3	50.1	0.8%
(Diluted)					
Drum 8	20.0%	Maximum	1.1	50.2	0.2%
(Diluted)					
Drum 8	19.5%	Minimum	3.3	50.2	0.6%
(Diluted)					
Drum 13	44.3%	Minimum	3.3	58.8	9.3%
Drum 13/14	42.3	Minimum	3.3	55.0	13.2%
(50% Each)					
8A Discharge	57.4%	Minimum	-	59.5	9.2%
	Drum 8 Drum 8 Drum 8 Drum 8 (Diluted) Drum 8 (Diluted) Drum 8 (Diluted) Drum 8 (Diluted) Drum 13 Drum 13/14 (50% Each)	Drum 8 33.6% Drum 8 33.6% Drum 8 33.8% Drum 8 29.8% (Diluted) Drum 8 20.0% (Diluted) Drum 8 19.5% (Diluted) Drum 13 44.3% Drum 13/14 42.3 (50% Each)	Tolids Depth	Toum 8 33.6% Intermediate 3.4	Toum 8 33.6% Intermediate 3.4 47.8

Drum 8: SiO₂ 4%, CaO 43%, S 19.9%, SO₂ 26%, SO₃ 17.2%, CO₂ 5.8%

Drum 13: SiO₂ 31.8%, CaO 18.2%, total S 7.5%, SO₂ 8.8%, SO₃ 8.0%, CO₂ 2.8%

^{*} One gallon is equivalent to 3.785 liters.

TABLE A20
(EL-030)

SUMMARY OF TVA SHORT-TERM CENTRIFUGE TESTS

Test Series	Machine Speed, rpm	Centrifuge Feed Source	Feed Rates, gpm ^c	Wt. % Solids in Feed	Wt. % Moisture <u>in Cake</u>	Wt. % Solids in Centrate
I	2000	HF clarifier bottoms	11-22	15-22 *	43-47	0.2-0.6
IIB	2000	HF clarifier bottoms	10-22	16-24*	44-46	0.3-0.5
III	2000	HF clarifier bottoms	10-22	19-29^	39-42	0.1-0.5
IV	2500	HF clarifier bottoms	9-33	19-27^	36-40	0.1-1.1
V	2500	Scrubber bleed (clarifier bypassed)	11-35	10-14	37-41	0.1-0.6

^{*}Increase the values by about 3 for pump seal water correction.

⁸Test Series II was a replicate of Test Series I.

^cOne gallon is equivalent to 3.785 liters.

TABLE A21

COMPARISON OF DEWATERING TECHNIQUES FOR LIMESTONE SCRUBBER SLUDGES

	Shawnee S	Samples	Western Power
Technique	Bulk Density (g/cm³)*	% Solids	Plant Samples % Solids
Clarification	1.14 <u>+</u> 0.02	20 <u>+</u> 0.5	~ 20
Settling	1.3 ± 0.04	40 <u>+</u> 0.5	50 (freely drained)
Centrifugation	1.4 ± 0.04	56 ± 0.5	> 65
Vacuum Filtration	1.6 ± 0.05	64 ± 0.5	> 65

^{*} The true density of Shawnee solids is reported to be $2.48~\mathrm{g/cm^3}$.

TABLE A22 (MI-084)

RESULTS OF TESTS OF SELECTED STABILIZED ROAD BASE MIXTURES PREPARED AT DULLES AIRPORT TRANSPO 72 PROJECT

Moisture	Dry ^a	Falling Head Permeabilities (cm/sec)
Content (%)	Density _(pcf)	7 Days
19.5	98.8	2.4×10^{-6}
19.4	98.1	N.D.*
20.0	98.3	2.9 x 10 ⁻⁶
19.8	98.2	6.5×10^{-6}
19.7	100.6	5.7×10^{-8}
20.0	98.8	1.0×10^{-6}
19.1	100.4	N.D.

^{*}N.D. - Not Determined

^aOne pcf is equivalent to 16,028 g per cubic meters.

TABLE A23

ATOMIC ABSORPTION TESTS FOR LEACHABLE IONS ON SELECTED SPECIMENS SUBJECTED TO 48 HOUR SHAKING TEST

(from MI-084)

	pH ¹	Total Dissolved Solids	Sulfate	C1	Al	Total Iron	Mn	Cu	Zn	Cd	Cr ⁺³	As	Нg	Pb	Sn
FEDERAL SPECIFICATIONS-MAX. 2	10.6	500	250	250	None	.3	.05	1.0	5.0	.01	.05	.01	.001	.05	None
Individual Solid Specimen															
Dulles Cylinder (13 Days) Dulles Cylinder (22 Days) Poz-O-Tec* Test Road Core Poz-O-Tec* Test Road	9.5 9.5 6.7	840 620 90	100 120 16	8 12 14	.38 .37 .03	.08 .08 .06	.18 .16 <.05	.08 .08 < .01	.02 < .01 < .01	<.01 <.01 <.01	.02 <.01 <.01	.02 .02 <.01	<.001 <.001 <.001	.08 .09 <.01	.10 .10 <.01
Cylinder Poz-O-Pac® Cylinder Fly Ash Concrete Cinder Block Clay Brick Asphalt Roofing Shingle	9.2 9.3 10.7 8.2 7.3 7.1	250 150 440 410 110 150	136 44 170 60 28 46	16 26 46 6 12 22	.05 .10 .22 .01 .03	.10 .25 .01 .04 .10	.10 <.05 <.05 <.05 <.05 <.05	.08 .08 .04 < .01 .01 < .01	< .01 < .01 < .01 < .01 < .01 < .01	<.01 <.01 <.01 <.01 <.01 <.01 <.01	<.01 <.01 <.01 <.01 <.01 <.01	.01 .01 <.01 <.01 <.01	<.001 <.001 <.001 <.001 <.001	.01 .02 <.01 .02 <.01 <.01	<.01 <.01 <.01 <.01 <.01
Aggregate															
Argillite Dolomitic Limestone Calcitic Limestone Steel Slag Aggregate Pumice Fly Ash-Sludge Aggregate Cement Mortar Balls Mine Tailings	6.9 9.75 8.4 10.8 7.1 11.7 9.0 3.95	120 96 180 840 120 700 530 130	28 8 8 16 < 1 < 1 27 6	22 18 - 28 10 16 8 2	.07 .02 .02 .05 .06 .03 .04	.06 .36 1.8 .15 2.2 .26 .17	<.05 <.05 <.05 <.05 <.05 <.05 <.05	.08 < .01 < .01 < .01 < .01 < .01 < .01 < .16	< .01 .02 .04 .02 .03 .02 .01	<.01 <.01 <.01 <.01 <.01 <.01 <.01	<.01 <.01 <.01 <.01 <.01 <.01 <.01	<.01 <.01 <.01 <.01 <.01 <.01 <.01	<.001 <.001 <.001 <.001 <.001 <.001 <.001	<.01 .07 .03 .01 .06 .06 .03	<.01 <.5 <.05 <.05 <.05 <.01 <.05
Loose Powdered Materials	0.0	0000	3500			0.0	. 05	. 01	0.1	. 03	. 01	4.03		06	
Fly Ash Portland Cement	9.8 12.0	2900 3700	1500 200	8 20	.11	.26 .44	<.05 <.05	< .01 < .01	.01 < .01	<.01 <.01	<.01 <.01	<.01 <.01	<.001 <.001	.06 .04	<.5 <.5
Water Samples															
Tap Water Snow Sample from Pittsburgh Water Supply (Peggs Creek)	7,5 6.45 7.25	180 40 316	< 1 -	76 6 -	.02 .06	< .01 .46 2.9	<.05 <.05 <.05	< .08 01 .05	< .05 < .01 .02	<.01 <.01 <.01	<.01 <.01 <.01	<.01 <.01 <.01	<.001 <.001 <.001	.04 .02 .02	<.01 <.01 <.01

With the exception of pH, all values are reported in parts per million.

Public Health Service Drinking Water Standards.

TABLE A24 PRELIMINARY LEACHING STUDY OF LIMESTONE SCRUBBING SLUDGE

LAB LEACHATE OF 2/28/73 FIELD CHEMFIX PRODUCT+

		Inches of Leachate Water°				
Constituent	Raw Sludge	0-25"	25 - 50"	50 - 75''	75-100"	
Aluminum (A1)	1.2	<0.10	<0.10	<0.10	<0.10	
Cadmium (Cd)	1.1	<0.10	<0.10	<0.10	<0.10	
Tot. Chromium (Cr)	0.8	<0.10	<0.10	<0.10	<0.10	
Iron (Fe)	760	<0.10	<0.10	<0.10	<0.10	
Nickel (Ni)	11	<0.10	<0.10	<0.10	<0.10	
Phenol	<0.25	<0.10	<0.10	<0.10	<0.10	
Cyanide (CN ⁻)	<0.10	<0.10	<0.10	<0.10	<0.10	
Zinc (Zn)	29	<0.10	<0.10	<0.10	<0.10	
Copper (Cu)	9.0	<0.25	<0.10	<0.10	<0.10	
Lead (Pb)	3.7	<0.25	<0.10	<0.10	<0.10	

All Results in ppm

^{+ =} Composite Material From Three (3) Disposal Cells

^{° =} Each 25" of Leachate Water Represents Approximately 800cc of Water

< = Less Than

TABLE A25

ATOMIC ABSORPTION TESTS MADE ON SURFACE RUNOFF OF A STABILIZED FLY ASH-SLUDGE MIXTURE

(from MI-084)

pH*	Total Dissolved Solids	Sulfate	C1	Al	Total Iron	Mn	Cu	Zn	Cđ	Cr ⁺³	As	Hg	РЪ	Sn
7.0	100	26	12	. 10	.22	<.05	<.01	<.01	<.01	<.01	<.01	<.001	<.01	<.01
6.9	96	32	18	. 15	.06	<.05	<.01	<.01	<.01	<.01	<.01	<.001	<.01	<.01
7.2	85	8	18	. 13	.06	.60	. 12	<.01	<.01	<.01	<.01	<.001	.03	<.01
	7.0 6.9	Dissolved Solids 7.0 100 6.9 96	Dissolved Sulfate 7.0 100 26 6.9 96 32	Dissolved Sulfate C1 7.0 100 26 12 6.9 96 32 18	Dissolved Sulfate C1 A1 7.0 100 26 12 .10 6.9 96 32 18 .15	pH* Dissolved Solids Sulfate Cl Al Total Iron 7.0 100 26 12 .10 .22 6.9 96 32 18 .15 .06	pH* Dissolved Solids Sulfate C1 A1 Total Iron Mn 7.0 100 26 12 .10 .22 <.05	pH* Dissolved Solids Sulfate Cl Al Total Iron Mn Cu 7.0 100 26 12 .10 .22 <.05	pH* Dissolved Solids Sulfate C1 A1 Total Iron Mn Cu Zn 7.0 100 26 12 .10 .22 <.05	pH* Dissolved Solids Sulfate Cl Al Total Iron Mn Cu Zn Cd 7.0 100 26 12 .10 .22 <.05	pH* Dissolved Solids Sulfate Cl Al Total Iron Mn Cu Zn Cd Cr ⁺³ 7.0 100 26 12 .10 .22 <.05	pH* Dissolved Solids Sulfate Cl Al Total Iron Mn Cu Zn Cd Cr ⁺³ As 7.0 100 26 12 .10 .22 <.05	pH* Dissolved Solids Sulfate Cl Al Total Iron Mn Cu Zn Cd Cr ⁺³ As Hg 7.0 100 26 12 .10 .22 <.05	pH* Dissolved Solids Sulfate Cl Al Total Iron Mn Cu Zn Cd Cr ⁺³ As Hg Pb 7.0 100 26 12 .10 .22 <.05

*With the exception of pH, all values are reported in parts per million.

TABLE A26

Pozzolanic Strength Determinations (kg/m²)

Molding Time	Shawnee Sample	Western Power PlantSample		
5 days	18,000 (26 psi)	119,000 (freshly demolded damp) (170 psi)		
1 month	18,000 (26 psi)	70,000 (dried over- night) (100 psi)		

TABLE A27

RESULTS OF TESTS OF SELECTED STABILIZED ROAD

BASE MIXTURES PREPARED AT DULLES

AIRPORT TRANSPO '72 PROJECT

(from MI-084)

Moisture Content (%)	Dry ^l Density	Compressive Strength ² at 100°F (psi)					
	(pcf)	2 Days	14 Days	28 Days			
19.5	98.8	301	732	881			
19.4	98.1	267	586	662			
20.0	98.3	369	630	889			
19.8	98.2	196	458	490			
19.7	100.6	333	772	861			
20.0	98.8	290	761	789			
19.1	100.4	200	868	1091			

 $^{^{1}}$ One pcf is equivalent to 16,028 g/m 3

 $^{^{\}circ}$ One psi is equivalent to 703 kg/m $^{\circ}$

TABLE A28

RESULTS OF FIELD TESTS SHOWING COMPARISON
OF POZ-O-PAC® AND POZ-O-TEC* FORMULATIONS

(from MI-084)

	⁴ Dry Densit y	⁵ Compressive Strength at 100°F (psi)		⁵ Strength of Cores from Road ¹ (psi)	
Description	(pcf)	2 Days	7 Days	4 Weeks	6 Weeks
Standard Fly Ash Mix (Poz-O-Pac*)	121.2	66	770	NCbs	NCP
Fly Ash-Sludge Blend A (Poz-O-Tec*) ³	121.4	348	729	NCP	1034
Fly Ash-Sludge Blend B (Poz-O-Tec*) ³	120.8	318	746	756	1089

¹Average temperature during curing period was 10°C.

²NCP - No core possible due to insufficient strength.

³Blends A and B not identified.

 $^{^4\,\}text{One}$ pcf is equivalent to 16,028 g/m^3

 $^{^{6}}$ One psi is equivalent to 703 kg/m².

APPENDIX B

LEACHING TESTS FROM SLUDGE DEPOSITS
PERFORMED BY STEAG-BISCHOFF
AT LÜNEN, GERMANY

August, 1973

1.0 INTRODUCTION

This paper describes the leaching tests from sludge deposits performed by Steag and Bischoff at Lünen, Germany. Steag-Bischoff are operating a lime based wet scrubber which treats a slip stream of the Kellermann steam plant at Lünen.

The information presented herein was obtained from Dr. Klaus Goldschmidt (Steag) and Dr. Kramer (Bischoff) during a visit at Steag in Essen. The report presents pilot tests performed during 1969 and field tests that started in 1972. No trace element analyses were performed. Of main interest was the build-up of sulfate, sulfite, total solids, the change of the pH and BOD and COD of the groundwater.

2.0 DESCRIPTION OF TESTS

The leaching experiments were done during the end of April, 1969, through August, 1969, on a pilot scale and from 1972 through the present in unlined pits close to the Kellermann steam plant at Lünen. Trace elements were of no concern during the two test series. The components of interest were sulfate, sulfite, cyanide, BOD, COD, pH, total solids and weight after ignition.

2.1 Pilot Experiments

The results of these experiments were presented by Dr. Klaus Goldschmidt at the Lime/Limestone Wet Scrubbing Symposium, March 16-20, 1970 in Pensacola, Florida. The goal of the tests was to find the effect of a permeable and impermeable ground soil and the effect of different thicknesses of the deposited slurry.

2.1.1 Description of the Pilot Setup

The setup for the pilot experiments (April through August, 1969) consisted of three tanks (see diagram in Appendix C). All tanks were of cylindrical shape. The diameter was 1 m and the height 0.5 m for tanks #1 and #2 and 1 m for tank #3. The sludge was filled upon gravel which rested on a sieve. Tanks #1 and #3 were continuously drained. Tank #2 was normally closed. Samples from tank #2 were taken once a week.

2.1.2 Results

The analysis of the sludge showed 14% CaO, 11% $SO_4^{\frac{1}{4}}$, and 2% $SO_3^{\frac{1}{3}}$ on a dry basis. Total water content of the wet sludge was 50%. (Consider the high degree of oxidation!) The total rainfall per m² during the test period was about 240 liters. The leachate was analyzed for calcium, sulfate, sulfite and pH (see Tables 1, 2, and 3 in Appendix C on pages 3 and 4 of the analytical results). The main conclusions drawn from these experiments were the following.

- 1. 20% of the rainwater passed through the deposit. 80% was lost due to evaporation during dry periods.
- 2. The amount of the total dissolved solids decreased continuously.
- 3. The total amount of leachate was greater at tank #1 then at tank #3. Therefore, it may be better to deposit the sludge in thick layers.

4. The total amount of the dissolved solids from tank #2 was highest and nearly constant over the test period. The sulfate content evidently did not reach the saturation point.

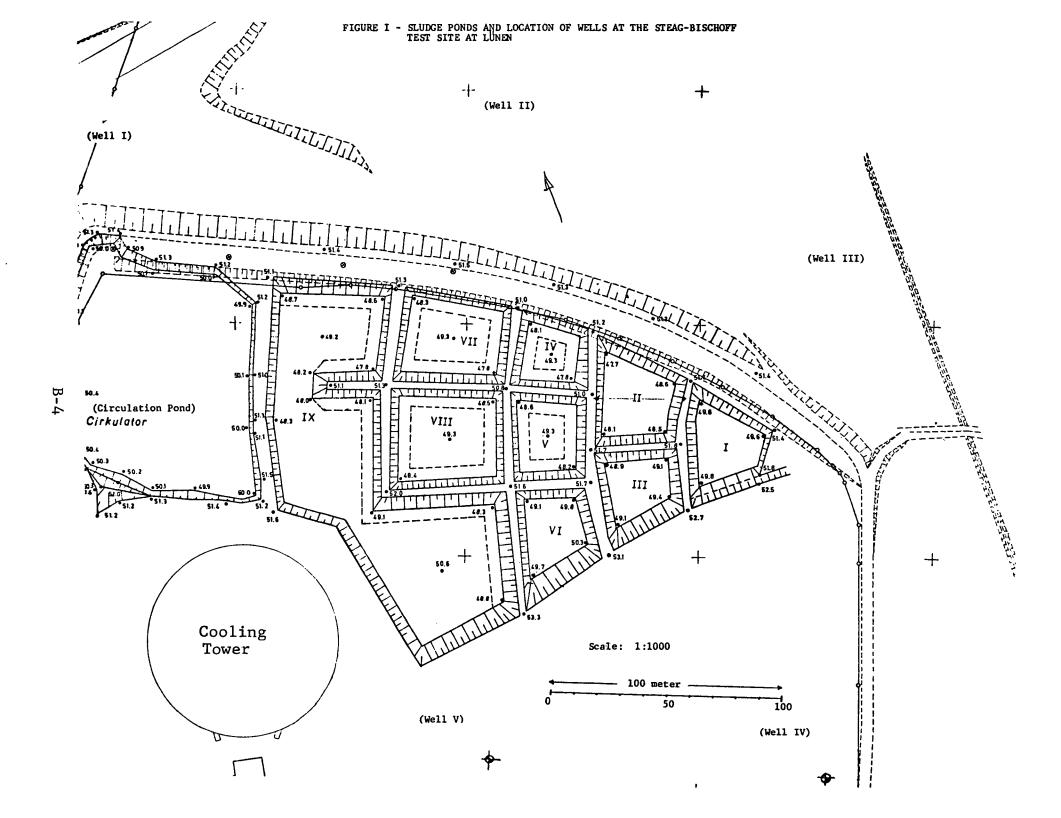
2.2 <u>Field Tests</u>

Bischoff is presently treating a slip stream at the Kellermann unit which corresponds to a 35 MW boiler. The sludge of the lime based scrubber is stored in ponds. The change in the groundwater composition is monitored by analysis of water samples taken from wells drilled around the storage site.

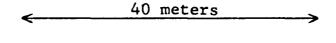
2.2.1 Description of the Pond Area

Figure I shows the location of the individual sludge ponds at the test site at Lünen. The scale is given on the diagram. The individual ponds show a dimension of about $40 \times 40 \,\mathrm{m}^2$. The ponds were filled with sludge starting with pond #1 at the right of Figure I. The figures in the drawing show the elevation of the corresponding points in meters above sea level. The cross-section indicated for pond #2 is schematically shown in Figure II.

The depth of the ponds is approximately 3.5 meters. The sludge is filled into the ponds up to 40-60 cm below the top of the dam. The ponds are unlined. The top soil consists of sand and gravel, then follows a silt layer. The groundwater table stands approximately 1 to 1.5 meters below the bottom of the ponds. It reaches either the silt formation or the sand-



Gravel Silt



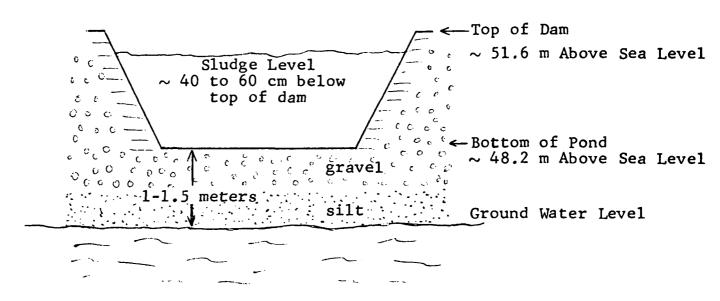


FIGURE II - SCHEMATIC CROSS SECTION OF POND NO. II

gravel formation. Thus, the pond is surrounded by very permeable material.

2.2.2 Slurry Composition

Appendix D shows the sludge analysis from August, 1972. Three interesting points are:

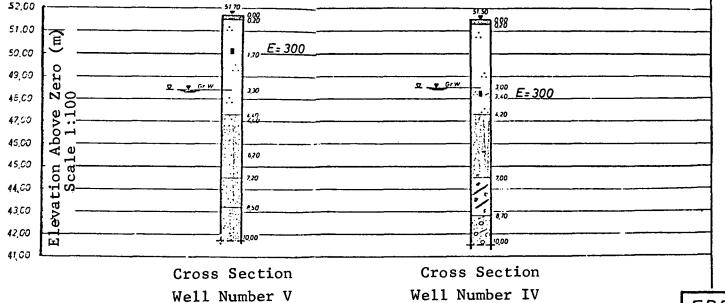
- The sludge was wet chemically analyzed for manganese. Manganese (oxidation catalyst) could not be found.
- 2. The degree of sulfite oxidation was only about 16%.
- 3. The high pH value of 9.8 (1 g sludge dissolved in 100 ml water) indicates free CaO in the sludge.

The low degree of sulfite oxidation is in contrast to the sludge found during the pilot experiments (11% SO_4^{-} and 2% SO_3^{-}).

2.2.3 <u>Description of Wells</u>

The locations of the wells are shown in Figure I. Until recently only wells No. I, II and III were monitored for groundwater pollution. The Water Quality Board insisted on the installation of two new wells, No. IV and No. V, which were drilled in March, 1973. The profile of the soil is shown in Figure III. The main difference between these two wells in comparison to wells No. I, II and III is the elevation of the





Formation Characterization

		Top Soil
		Coarse Sand
		Silty
		Fine Sand
		Coarse Silt
0		Silt
		Coarse Silt
		Sand
		Sandy
	** _F	Organic Matter
		Silt
	(F)	Gravel
Ž G-W		Groundwater Level
		Sampling Point

FIGURE III - PROFILES FOR WELLS NO. IV AND V

ERDBAULABORATORIUM ESSEN

Prof. Dr.-Ing. J.Schmidbauer Nachf. Dr.-Ing. H.Nendza - Obering. G. Morck 43 ESSEN • Susannastrafie 31 • Ruf 271054

Bohrprofile					1/2
Steag Bauv.: Bi			ellermann ,	Lünen	Bearb.Nr. 19245
Sachbearbeiter	gezeichnet	gepruft	Essen, den	Langen-Heffsteb	Mehen-Malistab
Lettgen	Blum		28.5.73	1: /	1: 100

groundwater table. Here it reaches sand formation and is about one to two meters higher than that of wells No. I, II and III. The exact height is shown in Table I.

2.2.4 <u>Analytical Results</u>

The analytical results from October, 1972 through April, 1973 are shown in Table II for wells No. I, II and III. The values reported in Table II are fairly constant and show no anomalies in comparison to the groundwater from other locations around Lünen. Results from wells No. IV and No. V are presently not yet available.

2.2.5 Conclusions

No conclusions can be drawn so far from the data collected; the main reason being that the groundwater movement was not considered at all. The average rainfall needs to be put in correlation to the groundwater movement from wells No. IV and No. V to wells No. I, II and III. If the groundwater movement is much greater than the average rainfall, one would not expect much of a solids build-up at all in wells No. I, II and III.

TABLE I
HEIGHT OF GROUNDWATER TABLE FOR WELLS NO. I - V

STEAG			5/076.54
	Measurement of Groundwater Leve	<u>1</u>	
	Date: 30-6-73		
	Measured by:	_	
Well l	Elevation of upper well casing	:	48,90 m
	Distance to groundwater	:	2,94 m
	Groundwater level	:	45,96 m
Well 2	Elevation of upper well casing	:	48,38 m
	Distance to groundwater	:	1,40 m
	Groundwater level	•	46,98 m
Well 3	Elevation of upper well casing	:	48,68 m
	Distance to groundwater	:	1,36 m
	Groundwater level	:	47,32 m
Well 4	Elevation of upper well casing	:	52,30 m
	Distance to groundwater	:	°3,40 m
	Groundwater level		48,90 m
Well 5	Elevation of upper well casing	•	52,52 m
	Distance to groundwater	:	3,68 m
	Groundwater level	:	48,84 m

TABLE II
WATER ANALYSES FOR WELLS NO. I, II, AND III

	Wel	1 1	Well	Well 2		. 3
	October 72	December 72	October 72	December 72	October 72	December 7
pH·	7,3	7,4	7,1	7,2	7 , 3	7,0
Dissolved Matter:						
Total (mg/l)	759	695	609	686	1273	845
Loss on ignition (mg/l)	#5 #	<u>ት</u> ትት	275	322	530	447
Potassium Permanganate Consumption (mg/1)	18	18	17	18	15	12
BOD (mg/1)	7	5	2	3	2	2
Sulfate (SO") (mg/l)	209	241	217	278	576	210
Sulfite (SO") (mg/l)	< 1	< 1	<1	∠1	८ 1	<u> </u>
Cyanide (CN') (mg/l)	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1

TABLE II (Cont.)

Wel	Well 1		Well 2 Well 3		3
Jan. 73	Febr. 73	Jan. 73	Febr. 73	Jan. 73	Febr. 73
7,2	7,9	7,3	7,8	7,1	7,3
752	928	731	778	940	-
526	<u></u>	469	_	568	-
14	25	16	13	12	14
Ţŧ	6.	3	3	3	3
241	284	197	223	214	221
< 1	<1	<1	<1	∠1	<1
∠0,1	<0,1	∠0,1	<0,1	∠0,1	∠0,1
	Jan. 73 7,2 752 526 14 4 241 <1	Jan. 73 Febr. 73 7,2 7,9 752 928 526 - 14 25 4 6. 241 284 <1 <1	Jan. 73 Febr. 73 Jan. 73 7,2 7,9 7,3 752 928 731 526 - 469 14 25 16 4 6. 3 241 284 197 < 1	Jan. 73 Febr. 73 Jan. 73 Febr. 73 7,2 7,9 7,3 7,8 752 928 731 778 526 - 469 - 14 25 16 13 4 6. 3 3 241 284 197 223 <1	Jan. 73 Febr. 73 Jan. 73 Febr. 73 Jan. 73 7,2 7,9 7,3 7,8 7,1 752 928 731 778 940 526 - 469 - 568 14 25 16 13 12 4 6 3 3 3 241 284 197 223 214 <1

TABLE II (Cont.)

	Well 1		Well	Well 2		3
	March 73	April 73	March 73	April 73	March 73	April 73
рН	7,3	7,0	7,3	7,0	7,4	7,1
Dissolved Matter:						
Total (mg/l) Loss on	1230	-	1090	-	1490	-
ignition (mg/1)	990	-	660	_	830	-
Potassium Permanganate Consumption (mg/1)	54	12	13	30	12	10
BOD (mg/1)	17	2	2	1	2	1
Sulfate (SO") mg/l	259	263	248	192	276	307
Sulfite (SO") mg/l	< 1	< 1	< 1	< 1	< 1	< 1
Cyanide (CN') mg/l	<0,1	<0,1	<0,1	< 0,1	<0,1	< 0,1

APPENDIX C

DEPOSIT-TESTS WITH LIME-FLY ASH-SLURRY OF THE WET SCRUBBER PILOT PLANT SYSTEM "BISCHOFF"

Prepared by:

Dr.-Ing. K. Goldschmidt
Steag

STEAG

Essen, den 11. 3. 1970 5/076.54 5/129

Deposit-tests with lime-fly ash-slurry of the wet scrubber pilot plant system "Bischoff"

by Dr.-Ing. K. Goldschmidt

presented at the lime/limestone scrubber symposium, March 16 - 20, 1970, Pensacola (Florida)

The strict regulations in West Germany, specially in the Ruhr-district, against water pollution forbid the deposition of flyash or other wellknown materials without the licence of the district water board.

It is therefore quite more difficult to receive the allowance depositing a new product like the slurry of a wet scrubber plant for desulphurizing and dust off waste gases of a power plant.

If you want to order such a prototype or fullscale plant the question of the possibility to deposit the slurry must be settled. Therefore a main point of our tests with the prototype scrubber plant, which is under construction, will be to control the influence of the deposited lime-flyash-slurry on the ground-water.

Our considered deposit area is a ground dip in a distance of about 500 m from the boiler- and scrubber-plant, surrounded by a street and a dam. Between the earth bank and the creek we intend to install three ground-water wells to control the quality of the ground-water. The layout of these wells is directed by the district water board and this authority will analyse the ground-water by itself once per month.

If the concentration of foreign substances in the ground-water surpasses the limit, we have the order to stop the deposit and eventually to remove the deposited slurry.

The start with ground-water analysis will be in May to find the zero conditions; the beginning of slurry deposit we assume during November this year.

To overlook what may happen, tentatively we set up three tanks, shown in <u>picture 1</u>, each with a cross-section area of 1 sqm. The bottoms of the tanks are conical with a drain tube in the middle Inside the tank, above the drain tube, are located a sieve, a fill of gravel and grit and the slurry.

The filling height of the slurry is 0.5 m in the tanks no. 1 and 2 and 1.0 m in the tank no. 3.

The drain tubes of the tanks no. 1 and 3 are permanently opened, so the slurry is always drained. The drain-water is sampled in a bottle separate for each tank. The drain tube of the tank no. 2 is normally closed and only opened during the water-sampling one time per week.

Thereby the tanks no. 1 and 3 represent the situation of slurry deposited with different bulk height on a region with water permeable ground, whilst the tank no. 2 demonstrates the condition of slurry deposit on a region with an impermeable ground to water.

The tanks were filled with slurry of the wet scrubber pilot plant system "Bischoff" at the end of April, 1969. The slurry had a water contents of about 50 % per weight. In relation to the dry substance

of the slurry we found about

After opening the valves in the drain tubes of the tanks no. 1 and 3, 10 % of the water contents of the slurry drained immediately (30 litres respectively 60 litres).

At the end of August, 1969, the total amount of rain per sqm ran up to 240 litres. 20 % of this amount of precipitate passed through the slurry and arrived at the bottles at the lower end of the tanks no. 1 und 3. 80 % of the rainwater was storaged in the slurry and recycled to the atmosphere by surface evaporation during dry weather periods.

During these four months the concentrations of the soluted substances in the drain water decreased continuously. The max. amounts at the beginning and the minimum at the end of August are shown in the following table:

Table 1: Analysis of drain water from tank no. 1 (concentrations in mg/l)

	max.	min.
CaO	1390	104
so ₄ "	185	5,3
so ₄ " so ₃ "	27	1,8
Hq	12	7,6

The analysis of the drain water from tank no. 3 produced the same concentrations.

The total amount of the substances washed out during this period shows <u>table 2</u>. In relation to the basic concentration of these components in the slurry the washing out amounts to

- 2 o/oo of the total contents of CaO) of tank no. 1 and 0,3 o/oo of the total contents of S)
- o/oo of the total contents of CaO) of tank no. 3
- 0,1 o/oo of the total contents of S)

In regard to these results it may be better to deposit the slurry in a thick layer than in a thin one.

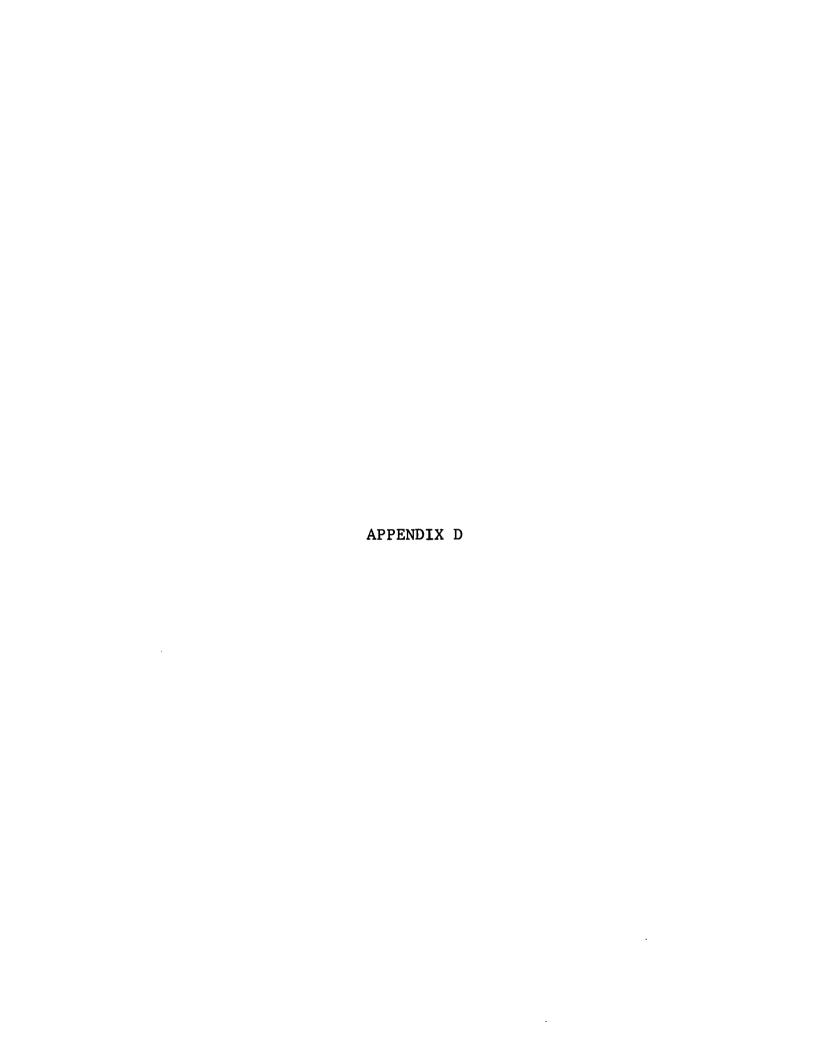
Table 2: Total quantity of washing out by rain (April - August 1969)

	tank 1	tank 3
CaO	77 g	97 g
so ₄ "	8 g	9 , 5 g
so 3"	1,9 g	1,6 g

Last not least the concentrations of the soluted substances in the water samples of tank no. 2 show more a constant than a decreasing tendency, see <u>table 3</u>. The amount of these concentrations gave no occasion to be concerned.

Table 3: Analysis of drain water from tank no. 2 (concentrations in mg/l)

	max.	min.
CaO	583	448
so ₄ "	372	180
ຣ ໐ູ້"	26	11,6
Hq	10.7	8,3



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Aktiengesellschaft

Development and New Facilities Department

ATTN: Dr. Goldschmidt

Your File No.: Your Letter Dated: Department/ Telaphone (Direct Date:

Our File No.: Dial):

5/076.54 8/15/72 UP2/Dr.Du/W 177-3969 9/25/72

Gs/Schu

Subject: BISCHOFF-PLANT IN LUNEN; SLUDGE ANALYSIS

Dear Dr. Goldschmidt:

You sent us a sample of the dried residue of the washing liquid used to desulfurize a flue gas component current in LUnen.

Due to the lime employed in the Lunen plant, the aqueous extract of your sample material shows an alkaline reaction. One gram of sample in 100 ml water shows a pH value of 9.8.

At 500 °C, the loss on ignition is 1.9%. At 800 °C it is 3.5%, while it equals 11.4% at 1100 °C. During the burning of the sample, we determined 2.0% organic carbon. In addition, we noted the development of 2.65% water of combustion, which is undoubtedly silicate-bonded water present in the hydroxide form.

A majority of the sulfur is present in the form of sulfite. Surprisinally, no carbonates were determined. Wet chemical analyses also did not detect an manganese.

Translated for Air Pollution Technical Information Center from the German

The sample showed the following composition:

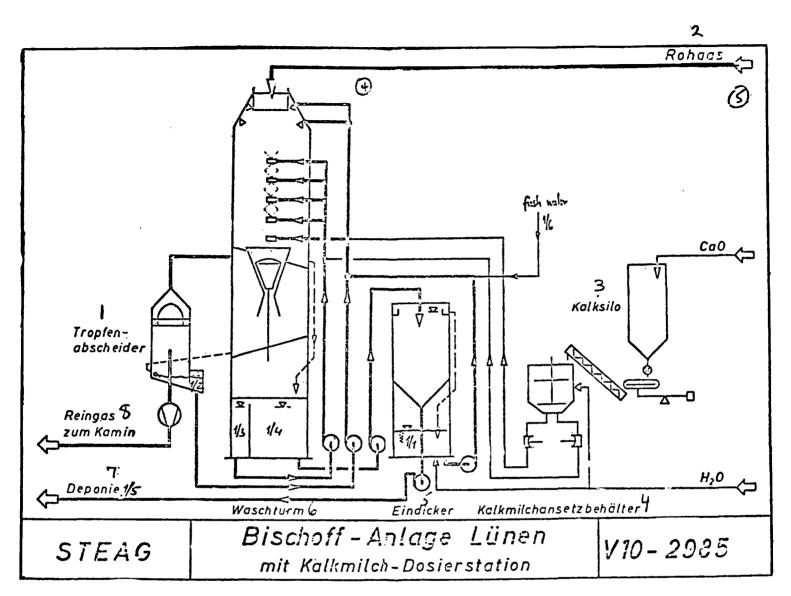
41.3%	SiO ₂
22.0%	A1203
0.9%	TiO ₂
7.4%	Fe ₂ 0 ₃
9.5%	Ca0
2.0%	MgO
0.8%	Na ₂ 0
4.2%	K ₂ 0
5.5%	SO ₂
0.8%	so ₃
0.02%	P ₂ 0 ₅
0.07%	F
0.15%	C1
2.65%	H_2^0 (water of combustion)
2.0%	C

Very Sincerely,
 RUHRKOHLE AKTIENGESELLSCHAFT
 (2 signatures illegible)

NUMERICAL TABLE 5

RESULTS OF THE CHEMICAL ANALYSES OF THE SUPERNATANT
LIQUIDS AND THE FRESH WATER

		Ca ²⁺	C1 ⁻	so ₄ ²⁻	SO ₂
<u>Sample</u>	pH Value	<u>g/1</u>	<u>g/1</u>	<u>g/1</u>	$\frac{mg}{1}$
1/1	7,4	1,64	3,30	1,35	10
1/2	2,8	1,72	3,23	1,46	14
1/3	7,5	1,95	3,30	1,26	16
1/4	7,7	0,19	0,67	mg/1 254	17
1/5	7,4	1,65	2,32	798	17
^D ω 1/6	9,1	mg/1 98	0,76	174	21
	_Mg ²⁺	Na ⁺	K ⁺	Total	Solids
1/6	22 mg/l	0,58 g/1	18 mg/1	1,7	g/1



STEAG Bischoff-Plant in Lünen With Lime Milk Dosing Station V10-2985

LEGEND: 1 = drop separator 2 = raw gas 3 = lime silo 4 = lime

milk application container 5 = thickener 6 = washing tower

7 = deposit 8 = pure gas to hearth

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4. TITLE AND SUBTITLE Evaluation of Lime/Limestone Sludge Disposal Options		5 REPORT DATE 19 November 1973		
		6. PERFORMING ORGANIZATION CODE		
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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The report presents results of a study of technology for disposal of sludge created by lime and limestone flue gas desulfurization systems at steam-electric power plants. Effects of operating variables on the volume of sludge produced are explained with emphasis on plant situations in the State of Ohio. Properties of sludges are reviewed, including settling characteristics, rewatering tendency, strength, particle size, bulk density, and chemical composition. The report considers potential environmental hazards of sludge disposal, namely contamination of water and ground water supplies. Methods of avoiding these hazards are presented and evaluated. Technologies for solidifying (fixating) sludge are discussed and evaluated along with the current status of full-scale projects. The report concludes that any large degree of commercial utilization is unlikely. Based on available data, there are no insurmountable problems in disposing of sludge in an environmentally acceptable manner. While economics of disposal are not well defined, studies are underway that should provide better cost information and other valuable information.

17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b.IDENTIFIERS/OPEN ENDED TERMS c. COSATI Field/Group		
Air Pollution Chemical Reaction Desulfurization Sulfur Dioxide Limestone Coal Sulfur	Sludge Disposal Calcium Oxides Combustion Products Flue Gases	Air Pollution Control Boilers Electric Power Plants	13B	
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