LONG TERM LYSIMETRIC LEACHING STUDIES OF FLUE GAS DESULFURISATION MATERIALS FROM THE COOLSIDE TECHNOLOGY.

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Abstract

Flue gas desulfurization materials generated by a commercial test of the Coolside duct injection flue gas desulfurization technology was emplaced under controlled compaction conditions in a field lysimeter. Leachates were collected over a period of three years and the soil gases were monitored, as were the changes in the mineralogical and geotechnical properties of the materials. The dominant early reactions include the hydration of anhydrite ($CaSO_4$) to gypsum and the formation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$). The dominant weathering reactions include the breakdown of gypsum and then ettringite through dissolution and carbonation reactions. The ultimate residual minerals being calcite and quartz. The original state of compaction was found to have a strong influence on the leachate chemistry with the highest compaction resulting in lower elemental concentrations and material wasteage. The leachates were composed primarily of Ca, Na, K and chloride and sulfate ions. The high pH's (10-12.5) favored the mobility of oxyanions.

Background and Methodology

This study was initiated during a successful test of the Coolside flue gas desulfurization technology at Ohio Edison's Edgewater generating station in 1991[1,2]. Coolside is a lime duct injection technology which is installed on the downstream side of the last heat exchanger. As tested by Ohio Edison, it also employs an alkali reagent, in this case NaOH, to enhance sulfur capture.

The overall goal of the this study was to develop sufficient chemical and physical data to insure the environmentally safe disposal of the material. The elemental release or leaching characteristics of the material was targeted for study.

Field studies included the controlled emplacement of the material under varying degrees of compaction in a field lysimeter (Figure 1). During the fill the geotechnical properties of the materials were measured. The lysimeters were excavated at the end of the project and the physical properties of the materials were again measured to determine the changes which had taken place.

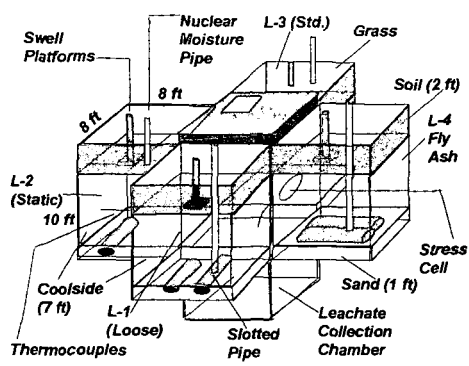

Figure 1. Diagram of Field Lysimeter.

The leaching properties of the material investigated included the determination of the chemistry of the leachate under laboratory column leaching and batch extraction (TCLP) conditions. The leachates from the field lysimeters were also collected and analyzed over a three and a half year period.

The physical and chemical properties of the materials are dependent upon complex mineral solution reactions. In an attempt to determine the overall controls on the system, detailed mineralogical determinations were made of the materials. Also, investigations were made into the state of the thermodynamic data available. A publicly available database and computer program was obtained from the United States Geological Survey and modified for this project[3].

Summary of Findings

Physical Properties of the Materials. Ninety-five percent (95%) of the Coolside material passed a 200 mesh sieve (-75 micron) and had a specific gravity of ~2.5. Index properties tests indicated that the Coolside materials were non-plastic and classified as ML (silt) in the Unified Classification System and A-4 under the ASSHTO System.

Table 1. Summary of chemistry from field leachates for first project year (March 1, 1993-February 28, 1994). Data in ppm except for pH and conductivity. Means not computed where more than 50% of samples were below detection limits.

	L1-3	N=44		L2-3	N=38		L3-4	N=52	
	Year 1	Year 1	Year 1	Year 1	Year 1	Year 1	Year 1	Year 1	Year 1
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Na	15767	5000	30000	15863	5300	33000	5480	3200	9100
Ca	800	335	1350	640	220	1340	45	18	90
K	5378	1640	8100	4764	1610	8000	1856	1000	3300
Al	ns	dl	dl	ns	dl	0.93	14.26	6.00	29.00
As	0.70	0.30	1.50	1.17	0.40	2.30	4.88	0.80	11.20
B	1.79	0.70	3.70	1.37	0.50	2.60	0.96	0.20	2.80
Ba	0.06	0.02	0.08	0.05	0.01	0.10	ns	dl	0.03
Cr	ns	dl	0.04	ns	dl	0.05	ns	dl	0.18
Fe	ns	dl	0.49	ns	dl	1.29	ns	dl	0.62
Mg	1.34	0.09	4.94	1.16	0.02	4.00	ns	dl	0.15
Mn	0.01	dl	0.04	ns	dl	0.05	0.03	dl	0.62
Mo	56.21	6.00	110.00	50.69	6.10	138.00	20.31	5.50	41.00
Se	2.44	0.30	3.70	1.85	0.25	3.55	1.09	0.24	2.00
Si	11.89	4.10	19.70	14.02	4.20	32.00	44.39	23.00	58.00
Ti	0.08	0.03	0.12	0.07	0.02	0.13	0.01	dl	0.02
V	0.54	0.28	0.98	0.85	0.07	1.80	1.56	0.92	3.47
Alk8.3	72	0	126	125	9	315	1905	275	4710
Alk4.5	186	139	314	249	143	550	3366	1573	7735
Cl	23908	1645	37590	23940	2380	46230	6897	2446	13200
Sulp.	17304	9000	20580	14311	2450	21410	2202	1214	3460
Br	nd	nd	nd	nd	nd	nd	1018	506	1960
pH	9.77	8.64	11.10	10.37	8.38	12.24	12.26	12.06	12.48
Cond.	70.18	19.40	102.00	66.21	19.80	108.30	28.56	14.90	48.50
D. Sol.	65677	16452	112500	59165	15772	107676	18462	8472	31122
S. Sol.	43	5	136	35	5	84	27	5	427

nd=not determined, ns=not significant, dl= below limits of detection

Table 2. Summary of chemistry from field leachates for third project year (March 1, 1995-March 29, 1996).

	L1-3	N=39		L2-3	N=26		L3-4	N=35	
	Year 3	Year 3	Year3	Year 3	Year 3	Year3	Year 3	Year 3	Year3
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Na	604	495	774	876	352	1635	1436	1035	2180
Ca	109	48	167	83	40	122	33	23	47
K	241	180	330	530	368	715	594	410	780
Al	0.47	0.20	0.92	1.11	0.45	1.74	12.69	10.50	16.20
As	0.30	0.21	0.44	0.47	0.15	0.77	1.16	0.85	1.60
B	0.57	0.30	0.85	0.68	0.30	0.95	0.21	0.05	0.48
Ba	0.01	0.01	0.02	0.02	0.01	0.03	0.01	0.01	0.02
Cr	0.01	0.01	0.03	ns	dl	dl	ns	dl	dl
Fe	ns	dl	0.28	ns	dl	0.20	ns	dl	0.12
Mg	ns	dl	0.10	0.06	dl	1.01	ns	dl	0.05
Mn	0.01	0.01	0.10	ns	dl	0.01	ns	dl	dl
Mo	0.93	0.52	2.00	1.36	0.61	2.90	3.40	1.75	5.00
Se	0.06	dl	0.11	0.09	dl	0.18	0.16	dl	0.45
Si	25.10	18.70	34.00	22.03	13.50	28.00	28.45	23.00	34.00
Ti	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.01
V	0.84	0.68	0.96	0.44	0.19	0.65	0.58	0.40	0.70
A8.3	129	0	262	144	66	258	563	288	920
A4.5	175	121	318	215	104	336	1033	799	1500
Cl	109	75	219	46	21	75	1408	838	2213
Sulp.	1506	1031	2052	2652	1671	5680	886	562	1510
Br	nd	nd	nd	nd	nd	nd	319	0	523
pH	11.15	10.95	11.34	11.32	10.91	11.54	12.00	11.84	12.19
Cond.	3.64	2.77	4.97	5.64	3.47	8.08	1.97	1.60	2.36
D. Sol.	2654	1850	3584	4276	2576	6870	5404	3872	7294
S. Sol.	5	5	10	5	5	5	6	5	25

Specimens compacted to 95% of maximum dry density (~1120 kg/m^3 or ~70 lbs/ft^3) and with optimum moisture (36.5%) were found to develop unconfined compressive strengths of between 1,000 psi and 2,500 psi (~6,900 to ~17,200 kPa). The compacted Coolside materials achieved permeabilities from 4 x 10^{-5} to 3 x 10^{-6} cm/sec (low to very low) in the lab.

Field Results. The field lysimeters were filled at three differing levels of compaction. Lysimeter L1 was loose filled (i.e. uncompacted) and had average dry density and moisture content of 706 kg/m^3 (44.1 lbs/ft^3) and 37.5%, respectively. Lysimeter L2 was compacted to the density designed to simulate the compactive efforts of a D9 bulldozer (117.3 kPa or ~17 psi). Dry density and moisture contents averaged 788 kg/m^3 (49.2 lbs/ft^3) and 38.9% in this lysimeter. The third lysimeter (L-3) was filled with Coolside material compacted near 95% of standard maximum dry density and optimum moisture content. Average values of dry density and moisture content were 1060 kg/m^3 (66.2 lbs/ft^3) and 37.0%, respectively.

After 3.5 years of weathering, the materials were excavated and their geotechnical properties determined. The average strengths of the materials in the three lysimeters were 44.1, 46.4 and 1,629 psi for the L1, L2 and L3 lysimeters respectively. Average permeabilities were 1.55 x 10^{-4}, 4.6 x10^{-4} and 2.2 x 10^{-6} for L1, L2, and L3 respectively. Thus, compaction had an overarching effect on the physical properties of the material. Achieving optimum compaction resulted in a fill which had substantial strength (layers of L3 achieved compressive strengths as high as 2,600 psi) and greatly reduced permeability (layers with permeabilities as low as 10^{-8} to 10^{-9} cm/sec were measured).

Mineralogy of the Materials The Coolside material as received was composed of quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), portlandite ($Ca(OH)_2$)), calcite ($CaCO_3$), hannebachite ($CaSO_3\ 0.5H_2O$) and minor anhydrite($CaSO_4$). A glassy phase is also present in the raw Coolside material and typically consists of spherical Si-Al fly ash particles. Upon hydration ettringite ($Ca_6Al2(SO_4)_3\ OH_{12}{\cdot}26\ H_2O$), the principal cementitious mineral in the system rapidly forms,

$$6Ca^{+2} + 2Al^{+3} + 3SO_4^{-2} + 12OH^- + 26H_2O = Ca_6Al_2(SO_4)_3OH_{12}\cdot 26H_2O$$

The state of compaction of the materials was found to have a strong impact on the chemistry of the leachates. Two distinct patterns emerged over the study. Lysimeters L1 and L2 initially had much higher elemental concentrations compared to L3 which was compacted to optimum density (Table 1). Sodium, Cl, K and sulfate were all higher in concentration by factors of 3 to 4 and Ca by a factor of more than 10 in L1 and L2 leachates. The longer term elemental release pattern showed a more rapid decline in elemental concentrations in the L1 and L2 leachates (Table 2). For example, Na in L1 dropped from an average value of 15,767 ppm--which is approaching the concentration of a brine--the first year, to an average value of 1,637 ppm the second year, and 604 ppm the third. The L3 leachates declined in concentration at a lower rate, with an average of 5,480 ppm the first year followed by averages of 2,302 ppm and 1,436 ppm the second and third year.

The leaching pattern for minor and trace elements did not necessarily show a similar pattern to that of the major elements. For example, Al and Si increased in concentration during the second year of the study in the L1 and L2 leachates as a function of pH of the leachates which increased over time.

The average pH of the L1, L2 and L3 leachates was 9.7, 10.4, and 12.3 during the first year of collection. Most transition metals are insoluble under these conditions and were not detected. However, elements which can form oxyanionic complexes such as Mo (MoO_4^{-2}), Se (SeO_4^{-2}), As (AsO_4^{-3}) and V (VO_4^{-3}) were found in measurable and sometimes significant concentration (e.g. Mo reached maximum concentrations >100 ppm in several samples the first year).

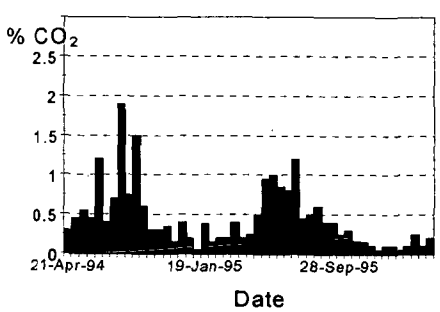

Figure 2. CO_2 Concentration in soil gas from 24 cm depth of lysimeter 1.

Carbon dioxide concentrations in the soil gases of the lysimeters were monitored in the second and third year of the study. In general, the highest CO_2 concentrations were reached during the summer and the lowest during mid-winter, as a function of respiration (Figure 2). The highest concentration recorded was 3.2% (32,000 ppm), well above that of atmospheric concentration (~350 ppm). Soil gas profiles gave clear and conclusive evidence of the highly reactive nature of the Coolside materials with respect to CO_2. At pH's above ~10 CO_2 reacts directly with hydroxide and forms carbonate ion,

$$CO_2 + 2OH^- = HCO_3^- = H^+ CO_3^{-2}$$

The thermodynamic analysis of the chemical composition of the leachates indicated that they are all supersaturated with respect to calcite and undersaturated with respect to gypsum and hannebachite. This, combined with direct mineralogical evidence, indicates that minerals are both dissolving and precipitating. The most important long term weather reactions include the precipitation of calcium carbonate and the dissolution of sulfites and sulfates, primarily hannebachite in this case, summarized as follows:

$$CaSO_3.1/2\ H_2O + 1/2O_2 + CO_3^{-2} = CaCO_3 + SO_4^{-2} + 1/2H_2O$$

Both the mineralogical and thermodynamic data indicate that ettringite will also break down over time. However this does not appear to proceed until the sulfate is largely exhausted. Thus, in effect, the sulfate acts as a buffer to extend the stability of the ettringite.

Elements of environmental concern which were found in concentrations exceeding RCRA limits included Se (RCRA limit 1 ppm) and As (RCRA limit 5 ppm). Some of the leachates from the L3 lysimeter reached concentrations as high as 19 ppm As during the first year of the study. The average concentration of Se for all of the leachates from the Coolside materials for the first year of study exceeded the 1 ppm limit.

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