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DETERIORATED CONCRETE FROM LINER OF WIPP WASTE SHAFT

by

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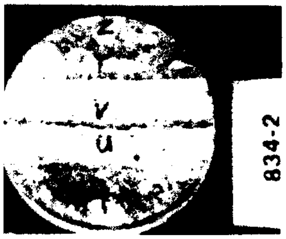

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13. ABSTRACT *(Maximum 200 words)*

Samples of a fly-ash concrete were studied after 6 years in service underground. The cores studied represented a construction joint and other areas of exposure to local groundwater. Observed evidence of deterioration, relative to companion cores of nondeteriorated concrete, included softening of the paste fraction, discoloration, an extensive network of microfractures cutting through both paste and aggregates, and crystalline deposits along fractures. In laboratory studies, we sought to determine the causes of these features, by studies of phase composition, chemical composition, and microstructure. X-ray diffraction analyses revealed magnesium chloride hydroxide hydrate, gypsum, and brucite in subsamples that should have been cement paste and along fractures. We attribute the condition of the concrete to chemical alteration by interaction with magnesium-bearing groundwater, which occurs naturally in the service environment.

14. SUBJECT TERMS

Brine	Magnesium	Waste Isolation Pilot
Concrete	Portland cement	Plant (WIPP)
Deterioration		

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PREFACE

The work described in this report is part of an ongoing research effort accomplished in the Concrete Technology Division (CTD), Structures Laboratory (SL), US Army Engineer Waterways Experiment Station (WES), under contract to Sandia National Laboratories (SNL), Albuquerque, NM. Dr. E. J. Nowak is Technical Monitor for SNL for this project. The laboratory studies at WES were completed under SNL Document No. 69-1729, as directed under Federal Agency Order 101-KF5 (11-88) for the US Department of Energy.

Laboratory studies for the report series were accomplished in CTD, during June through December 1990, with direct guidance from Dr. Lillian D. Wakeley, Acting Chief, Engineering Sciences Branch, CTD. Mr. J. Pete Burkes coordinated the hands-on laboratory work, with assistance from Ms. Judy C. Tom and Mr. Terrence Tolliver. Dr. Toy S. Poole contributed to the analyses of EDX data and interpretation of all data. Messrs. Dennis L. Bean, G. Sam Wong, and Donald M. Walley also assisted. Drs. Nowak and Steven Lambert, SNL; Menashi D. Cohen, Purdue University; and Mr. Bryant Mather, Director, SL, WES, contributed to technical discussions and interpretation. Drs. Wakeley and Poole and Mr. Burkes prepared this report.

All ideas and activities attributed to the first person plural, "we," are those of people in the Concrete Technology Division, unless otherwise indicated.

This project was completed under the general supervision of Mr. Mather; Mr. James T. Ballard, Assistant Director, SL; Mr. Kenneth L. Saucier, Chief, CTD; and Dr. Wakeley. Dr. Wakeley was principal investigator.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander and Deputy Director was COL Leonard G. Hassell, EN.

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CONVERSION FACTORS, NON-SI TO SI (METRIC) UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
Fahrenheit degrees	5/9	Celsius degrees or kelvins*
feet	0.305	metres
inches	25.4	millimeters
pounds per square inch	0.006894757	megapascals (MPa)
pounds (force)	4.448222	newtons

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* To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: $C = (5/9)(F - 32)$. To obtain Kelvin (K) readings, use: $K = (5/9)(F - 32) + 273.15$.

DETERIORATED CONCRETE FROM LINER OF WIPP WASTE SHAFT

PART I: BACKGROUND

1. In May 1990, Dr. E. J. Nowak of Sandia National Laboratories (SNL) requested Waterways Experiment Station (WES) under FAO 12-9829 and specifically Dr. L. D. Wakeley and staff of the Structures Laboratory (SL), Concrete Technology Division (CTD), to analyze samples of apparently deteriorated concrete and identify deterioration mechanisms. The samples were taken from the liner of the waste handling shaft at the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico. The objectives of this major laboratory research effort at WES were to determine the condition of the deteriorated concrete and identify probable mechanisms of deterioration. The results were used to assist in evaluating the status of the liner and the need for any remedial action. This report provides necessary background, summarizes the results, and presents possible mechanisms for the degradation process.

The WIPP and Organizations Involved in this Work

2. The WIPP was authorized by Public Law 96-164 "as a defense activity of the DOE [Department of Energy] for the express purpose of providing a research and development facility to demonstrate the safe disposal of radioactive wastes from the defense activities and programs of the United States." The WIPP will demonstrate the disposition of defense transuranic (TRU) wastes now stored at and being generated by various DOE facilities and will perform radioactive and nonradioactive tests to understand the behavior of TRU waste in bedded salt.

3. SNL will support the DOE by providing a detailed geotechnical understanding of the WIPP Site, scientific research on issues related to disposal of defense TRU wastes in bedded salt (necessary to provide data for performance assessment calculations), and detailed performance assessment research to evaluate compliance with the Environmental Protection Agency (EPA) standard

(Code of Federal Regulations, Title 40, Part 191, Subpart B) for geologic repositories. SNL is a technical adviser to the DOE.

4. Westinghouse Electric Corporation (WEC) is currently the operating contractor for the WIPP. The Waste Isolation Division (WID) of Westinghouse is currently carrying out the work of the operating contractor.

5. The Concrete Technology Division (CTD), Structures Laboratory, Waterways Experiment Station (WES; Corps of Engineers, Department of the Army) has provided support for the SNL effort on WIPP in the form of the selection of components and proportioning of cementitious grouts and concretes for in situ tests and for studies of the geochemical stability in the WIPP environment of cementitious materials. In particular, WES supported Series A and B of the Small-Scale Seal Performance Tests (SSSPT) (Stormont 1985) in which salt-saturated concrete was emplaced at the WIPP disposal horizon in both horizontal and vertical 1 m diameter boreholes to validate the emplacement methods and performance of concrete formulations in both horizontally and vertically oriented excavations.

The Concrete Liner of the Waste Shaft

6. Design information and construction history for the Waste Shaft are given in the WIPP Design Validation Final Report (U.S. Department of Energy 1986). The Waste Shaft was designed to function throughout the operational period of the WIPP (approximately 30 years) (U.S. Department of Energy 1986). The following is a summary of design and construction information for the Waste Shaft liner.

7. The concrete liner of the Waste Shaft was placed during the period from November 1983 to April 1984. Typically, liner concrete was placed in 24-ft* lifts following each 30-ft-long enlargement of the shaft from the original diameter of 6 ft to the current 20 ft. The liner was constructed from the surface downward to a depth of approximately 830 ft. Then, during the last week of March and the first week of April 1984, the liner key was constructed upward from a depth of approximately 900 ft to approximately

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* A table of factors for converting non-SI units of measurement to SI (metric) is presented on page 3.

830 ft in lifts, each being 8 to 10 ft. Thus, more than two weeks elapsed between placing of the concrete at the bottom of the liner and placing the concrete at the top of the key. In addition, the concrete at the top of the key was poured underneath the previously poured liner, adding complexity to the task of forming a tight joint between liner and key. This joint will be described in paragraph 18 as a focus for studies of degraded concrete. For geologic orientation, the joint at the top of the key is near the contact between the Rustler and Salado Formations. Figure 1 shows the approximate configuration of the shaft liner (not to scale) and enclosing geologic formations.

8. The concrete for the Waste Shaft liner and key was specified by Bechtel National, Inc., the architect/engineer in Specification 03300-1FB/01D. The aggregate was specified to conform to ASTM C 33 and was supplied from local commercial quarry operations in the Carlsbad, New Mexico, area. The specified cement conformed to ASTM C 150, Type V. This concrete formulation can be described generally as a mixture of low-alumina cement, a pozzolan, and an aggregate, with a low ratio of water to cementitious materials. Additional details of concrete specification and materials are in Appendix A.

9. There may have been sand-rich mortar applied to the inner surface of the liner for cosmetic reasons. Detailed information on materials and procedures that may have been used for topical application of mortar to the Waste Shaft liner is not available.

10. Three water collection rings were installed on the inner surface of the liner to measure and aid in the control of any liquid flowing down this surface. Two rings were located in the Rustler Formation, one below the Magenta and one below the Culebra water-bearing zones of the Rustler Formation. The third ring was located at the bottom of the liner key in the Salado Formation.

11. Two grouting programs using both cement-based and chemical grouts were carried out by grout injection through grouting pipes into the space behind the liner to control liquid inflow. The first grouting was done following the completion of the liner and key and was reported by Bechtel (1985). The second grouting was two years later after liquid leakage into the shaft was observed (Dynatec Mining Corporation 1988).

Observations of Degraded Concrete On the Surface of the Waste Shaft Liner

12. During inspections of the Waste Shaft in May 1990, patchy areas of apparently deteriorated concrete or surface mortar were observed between approximately 810 ft and 900 ft below the surface. Weekly inspections are normal for the Waste Shaft, but such inspections were suspended during the period from 18 July 1989 through April 1990 while the WIPP Waste Shaft hoist bearings were being repaired (Westinghouse Electric Corporation 1990). Apparently, the process of surface deterioration had progressed sufficiently during the nine-month period of suspended inspections that deterioration was visible during next shaft inspection in May. DOE, WID, and SNL personnel observed the deteriorated areas on the inner surface of the shaft liner and noted increased deterioration and possible seepage of groundwater at joints in the liner key, particularly at what appeared to be a joint located 834 ft below the surface. They collected grab samples of areas of deteriorated material near this joint. The samples were brown in color and soft enough that it was possible to remove a layer about 1/4-in. thick from the surface of the concrete using hand tools.

13. On 25 May 1990 and during the following week, SNL received some of the grab samples of concrete from the liner surface and also of liquid from the collection ring at the bottom of the key. Normal sample control documentation was not completed for these grab samples, because they were intended only for short-term informal (scoping) studies to aid in planning a formal investigation. Scoping analyses of these grab samples were carried out at SNL and portions of them were also sent to WES for inspection. The results from these scoping studies and inspections were used to develop preliminary working hypotheses, to plan and request core sampling from the Waste Shaft liner, and to plan the initial investigative work at WES. Cores samples from the liner between joints and at the joint (including material from the joint) at a depth of 834 ft were requested by SNL and WES.

14. Subsequently, SNL provided core samples of waste-handling-shaft concrete to WES for laboratory studies to determine properties of the degraded concrete and the extent and mechanisms of deterioration. The next part of this report describes these core samples and outlines the sampling history.

The remaining parts provide results of the analyses. The working memos provided to SNL by CTD during this work are reprinted in Appendix B.

PART II: SAMPLES OF WASTE SHAFT LINER CONCRETE PROVIDED TO WES: SAMPLE IDENTIFICATION, LOCATIONS, AND HISTORICAL SUMMARY

15. Samples were identified in the field by depth from the surface and by a suffix to differentiate among samples taken at the same depth. For samples from 812 and 890 ft, suffixes to the depth in ft are the horizontal angular orientation from true north (000 degrees). For example, a sample designated by 812-265 is a sample taken at 812 ft below the surface (below the top or collar of the shaft) and 265 degrees clockwise from true north. Core samples from the other depths were numbered by depth in ft and assigned consecutive suffixes.

Core Samples from the Surface of the Concrete Liner at Depths of 812 and 890 ft

16. Core samples approximately 6 in. long (6 in. into the concrete from the open surface of the liner) were obtained at depths of 812 ft and 890 ft. Two core samples from 812 ft (identified as 812-265 and 812-340) and one core sample from 890 ft (identified as 890-265) were shipped to WES on 8 June 1990. These core samples are listed in Table 1. The analyses of these core samples performed by WES are described in Part IV of this report. Details of these analyses are given in Appendix C.

17. Results from the WES analyses of these core samples revealed several plausible mechanisms of surface concrete deterioration: acid attack (possibly due to carbon dioxide absorption in groundwater on the inner surface of the liner); cracking due to cyclical wetting and drying and crystallization in cracks; chemical alteration of cement paste by reaction with brine; or combinations of these mechanisms that interact to make the concrete more susceptible to attack by all mechanisms. The multiplicity of mechanisms, some requiring exposure at the surface to ventilation air from which carbon dioxide could be absorbed and into which water could evaporate (drying), highlighted the need for core samples of the construction joint where there could be no direct exposure to ventilation air. We reasoned that analyses of samples taken from along an apparently leaking joint would reveal any deterioration that might be attributable to the liquid. They could help us differentiate among mechanisms and reveal whether deterioration was occurring at locations

isolated from exposure to air. SNL and WES agreed that additional impetus now existed to obtain cores from the cold joint at 834 ft, and appropriate coring was requested.

Cores Samples from the Cold Joint at 834-ft Depth

18. Three core samples of the joint at a depth of 834 ft were taken on 15 August. The cores were approximately 6 in. long. Two cores from that location (identified as 834-1 and 834-2) were shipped to WES for analyses. These cores are listed in Table 2. The third core (identified as 834-3) was shipped by WID to Lankard Materials Laboratory, Inc. The results of the Lankard analyses are described in a report (Lankard Materials Laboratory, Inc. 1991).

19. WES analyses of the core samples containing the joint at 834 ft showed layers of deteriorated concrete approximately 20 mm thick above the joint and approximately 50 mm thick below the joint. The cement paste in the layers of deteriorated concrete lacked the necessary strength and bonding characteristics required for structural concrete. The aggregates also were deteriorated (softened and fractured). Although cycles of wetting and drying could have led to observed crystalline deposits in fractures, carbon dioxide absorption leading to acid attack could not have contributed significantly to the deterioration that was observed in the joint. These observations, coupled with analyses of phase composition and micro-structure, led to the conclusion that deterioration probably was attributable to chemical interactions between dissolved species in intruding groundwater and the components of the concrete. Therefore, WES and SNL agreed that deterioration behind the liner was possible and should be investigated by study of core samples through the full liner key thickness to the liner key/host rock interface. Full thickness core samples were requested.

Core Samples Through the Concrete Liner Key from Just Above (832 ft) and Just Below (836 ft) the Cold Joint at 834-ft Depth

20. Two full-thickness cores of the Waste Shaft liner key were obtained, and core segments that included the outside surface of the concrete

liner key and material encountered behind the liner were received by WES on 2 November 1990. The cores were taken just above (at a depth of 832 ft) and just below (at a depth of 836 ft) the joint at 834 ft. WES received three core segments from the lower core (identified as 836-1/3, 836-1/4, and 836-1/5) and one core segment from the upper core (identified as 832-1/3). Samples of clay-like material from the interface end of the upper core were also received. These core segments and clay-like materials are listed in Table 3.

21. Deteriorated concrete was found at the end of each core representing the surface of the concrete behind (on the host-rock side of) the liner. This deteriorated zone was similar in thickness and physical and chemical characteristics to the layers above and below the joint at 834 ft, as determined by analyses of the core samples taken at 834 ft.

22. The following parts of this report present relevant published results from other investigations, more detailed summaries of the analytical results, and descriptions of probable degradation mechanisms.

PART III: CHEMICAL INTERACTIONS BETWEEN AGGRESSIVE IONS AND CEMENTS

Previous Studies

23. A search for previous work on magnesium attack on concrete yielded abundant information about this phenomenon for concrete in seawater. Initially, this previous work seemed applicable to the waste shaft concrete. Mather (1966) wrote:

> Concrete exposed to seawater is wetted by a solution of salts -- principally sodium chloride and magnesium sulfate. Damage to concrete, if it occurs, usually results from failure to use good practices in concrete construction, and often is the result of freezing and thawing or wetting and drying, as much as or more than the results of the effects of seawater as such. Magnesium sulfate may attack most, if not all, of the constituents of hardened portland cement paste, especially the aluminate constituent; chlorides may promote corrosion of steel; alkalies may participate in alkali-aggregate reactions. Thus, concrete exposed to seawater should be made with cement of controlled aluminate content and with nonreactive aggregate, embedded steel should be well covered by concrete of low permeability, and good construction practices should be followed.

24. With a closer look at the mechanisms listed for seawater attack on concrete, we realized that such studies give only a vague parallel to the concrete in the waste shaft. This concrete liner experiences no cycles of freezing and thawing and may be subjected to wetting and drying only on its inner circumference. The liner was largely unreinforced concrete, so corrosion of embedded steel was not a factor in deterioration. No reactive silica was identified in the aggregate, precluding classic alkali-aggregate reaction. Alkali-carbonate reaction may have occurred, and the carbonate rock aggregates were softened and cracked, but the paste was in even worse condition than the aggregates. This leaves attack by magnesium sulfate as the most probable cause of deterioration.

25. Studies of seawater effects on concrete became even less appropriate when we considered the total chemical composition of the fluid recovered from the brine collector ring. The concentration of magnesium and of total dissolved solids was far higher in the waste shaft brine than was that of any experimental or natural seawater or brine in any of the published work we

considered. The chemical activity of the WIPP waste shaft environment is unique (chemical composition of brines summarized in memo from S. Lambert, 15 February 1991).

The Mechanism of Damage

26. Cohen and Bentur (1988) reviewed the damaging effects of magnesium sulfate and sodium sulfate solutions on portland cement pastes. They wrote: "The greater damaging effects of ... magnesium sulfate solution on portland cement ... specimens are due to the decomposition of the C-S-H gel to M-S-H -- magnesium silicate hydrate -- which is noncementitious." C-S-H is the desired strength-giving calcium silicate hydrate of normally cured portland cement.

27. In environments unaffected by sodium chloride, C-S-H reacts with magnesium sulfate to produce gypsum and magnesium hydroxide plus silica hydrate. The gypsum reacts with calcium aluminates to make ettringite. The magnesium hydroxide and silica hydrate produce the noncementitious magnesium silicate hydrate. This phase has long been known to form at ordinary temperatures in the breakdown of portland cement in the presence of soluble magnesium salts (Cole 1953). Where sodium chloride also is abundant, as in the WIPP waste shaft, gypsum remains as gypsum, and calcium aluminates combine with available chlorides to form calcium chloroaluminate (Massazza 1985; Ftikos and Parissakis 1985). Magnesium hydroxide and silica hydrate may form magnesium silicate hydrate, but under some conditions they may remain or form other poorly crystalline compounds. In either case, this phase assemblage makes a very low-strength concrete.

28. The experimental work of Cohen and Bentur (1986) included exposure of Type I and Type V (sulfate-resisting) and other cement pastes to solutions of sodium and magnesium sulfates. They monitored chemical and physical attack as indicated by mass change, compressive strength, and phase composition. Their results showed that pastes exposed to magnesium sulfate solutions softened and disintegrated as the M-S-H formed. The supposedly sulfate-resistant Type V was nearly as susceptible to this degradation mechanism as was the Type I portland cement. In both cases, reduction in strength and mass occurred without appreciable expansion, making this deterioration mechanism fundamentally different from the classic "sulfate attack" widely documented in

concrete studies (Buck, Mather, and Mather 1984; Buck 1988; Wong and Poole 1988; Ouyang 1989; Harrison 1990; Cohen and Mather 1991; and many others).

29. Oberste-Padtberg (1985, 1986) determined that the chemical attack on concrete by magnesium compounds was most severe in environments providing exposure to magnesium and calcium chloride. He stated: "The common effect of both calcium and magnesium chlorides is a drastic decrease in the pH at the brine-cement interface. This leads to C-S-H decay and, consequently, to ...cement degradation." The calcium silicate hydrates formed from normally cured portland cements are chemically stable only at pH 12.5 and higher.

30. Several studies, such as those cited by Biczok (1972) and those of Oberste-Padtberg (1986), Harrison (1990), and Ftikos and Parissakis (1985), conclude that the attack of magnesium compounds on concrete is diminished by the presence of abundant sodium chloride. Others, including Ben-Yair (1974), conclude that the deleterious effects of magnesium sulfate are not diminished by the presence of sodium chloride, although he does not address the effect of magnesium chloride specifically.

31. We have very little basis to judge whether or not to apply the conclusions of published research to the WIPP environment. Virtually no other study reports the interaction of a solution with a chemical composition as complicated and an ionic strength as high as those of the brine from the WIPP waste shaft collector ring. It is clear that the degradation mechanism involves chemical interactions between brine and concrete. Further, the resulting phase composition and properties of the affected concrete are similar enough to various aspects of the results of these previous studies to indicate that these same mechanisms of degradation are among those that altered the waste-shaft concrete. None of the previous work we reviewed entirely explains this geochemical system.

32. We found no reference in any other study of the formation of the phase magnesium hydroxychloride hydrate in a concrete affected by seawater or brine. Yet this phase was perfectly crystallized and abundant in fractures and on other free surfaces where the cement showed the most severe deterioration, and especially in joint-fill material. The scope of the work reported here did not include isolating the appropriate variables of chemical composition to prove the exact chemical mechanism of degradation.

Other Comments About the Brine and the Joint-Fill Materials

33. Data from Steven Lambert of SNL (memorandum of 28 June 1990) indicated that the amount of magnesium in the brine from the collector ring, and by inference the brine along the 834 joint, was higher than could be explained by locally available groundwaters. Also, the chloride level was higher than could be accounted for by matching it to the level of sodium and assuming halite to be its source. In discussions with Dr. Lambert, we considered the possibility of a man-made source for either magnesium or chloride, or both, from some component of the shaft liner system.

34. One possible explanation for the high magnesium content in the collected brine is that sorel cement might have been used. This material is a magnesium oxychloride. Its hydration reactions are complex and nonsequential and involve formation of various magnesium carbonates and hydroxycarbonates. Formation of these carbonates is enhanced by addition of many organic and inorganic compounds, including calcium sulfate-silicate mixtures. This material has been used for temporary plugging of wells in the oil industry because it has a lower modulus than hydrated portland cements and resists accumulated static loads (Bensted 1989). Sorel cement also has been used with additives that are purported to give it better resistance to magnesium sulfate, a useful property in stopping brine flow in wells. These cements are intended for temporary use and are easily removed with acid solutions.

35. Sorel cements are not concrete materials, and WES has no recent experience with their use. However, many disadvantages are reported for this family of cements. They have poor dimensional stability. The hydroxychloride hydrates are water soluble and release corrosive solutions (Bensted 1989). The phase composition of sorel cement hydrated in brine is not well documented or well understood, and many of the compounds that form are chemically unstable. Very high-concentration brines may decrease both strength and stability (Gillen 1991), possibly by causing it never to set. Setting and strength properties are unpredictable in mixtures with both: 1) calcium sulfates and silicates (used to enhance carbonate formation as mentioned previously); and 2) chemically complicated and strong brines, such as those available in the waste shaft. There is, however, no direct evidence for the use of sorel cement in the joint. WES geochemical studies during May-Sept 1991 revealed that

magnesium hydroxychloride hydrate does form in reactions between simulated WIPP high-Mg brine and portland cements.

36. We also considered the possibility that a calcium chloride accelerator had been added to grouts pumped into the annulus, as suggested by Galbraith (1990). Grout saturated with sodium chloride may have been used to fill a gap at the annulus between the concrete liner and the host rock. WES experience has demonstrated that such a grout could require more than one day to set. If this long delay was considered unacceptable, use of a calcium chloride accelerator might have seemed like a simple way to hasten setting. (WES does not recommend this combination of materials.) This is another potential man-made source of a high chloride content in the brine, unaccompanied by equally high sodium.

PART IV: ANALYSES OF 812 AND 890 CORES

Selection of Samples for Study

37. The first of the three groups of samples analyzed at WES was selected by WIPP site staff. Samples had been selected to represent areas showing apparent discoloration or deterioration on the inner surface of the shaft liner or areas where the wall was wet. Samples included three sections of core, two from 812 and one from 890; three bags of loose granular material (grab samples) removed from the inner surface of the shaft liner, two at 812 and one at 890; and a sample of brine from the collector ring at the bottom of the liner. See Table 1 for identification and descriptions. The core from 890 at 265 was taken from a wet area 4 in. below a construction joint at which water was apparently entering the liner opening and running down its inner wall.

38. The initial studies of grab samples were inconclusive because we knew so little about the original concrete (we received data from batch tickets and other details from SNL in September 1990, after the first and second sets of analyses were complete. We did not learn the details of the materials that were used for modifications [repairs] to the liner while in service). The grab samples were so different from each other and from the cores of intact concrete that we assumed they were samples of grouts or other materials that may have been applied locally as a surface coating on the concrete for nonstructural reasons. One sample contained no coarse aggregate. Only one grab sample corresponded directly to a core segment (from 812-265). The question of the topical or cosmetic application of grout was never resolved. We based no major conclusions on the results of analyses of the grab samples.

Analytical Techniques and Subsampling

39. Our task included determining the current condition of apparently deteriorated concrete and that of apparently "good" concrete (represented by most of the length of each core), and from this postulating the cause of deterioration. Because only the ends of each core appeared deteriorated, we could not compare two sets of physical properties, such as compressive strength of

"good" and "bad" concrete. WES tested the compressive strength of the "good" portion of one core segment (812-265), and it was approximately 9,000 psi. The deteriorated material could be broken in your fingers.

40. Most of our analyses centered around standard techniques of forensic petrography, including visual description, phase composition by X-ray diffraction (XRD), petrographic examination at various magnifications, and scanning electron microscopy coupled with energy-dispersive X-ray analysis for chemical composition. We selected subsamples for intense study from many individual components of the as-received samples: aggregates from cores and grab samples; crystalline coatings on these aggregates or on sockets where aggregates had been; samples sieved from the paste portion of concrete (called paste concentrates), from both intact and damaged areas; small pieces of debris and discolored areas; hand-picked individual crystals from grab samples and elsewhere; sediment from the brine; and other interesting bits. Appendix C of this report gives more detail about subsample selection and preparation, and about forensic analytical techniques.

Results of Analyses

41. The exposed ends of cores taken from 812 ft were darkened and discolored to a depth of 2 cm (see core 812-265 in Figure 4). The darkened portion was strongly hygroscopic. It became wet-looking within minutes of being initially unwrapped in an air conditioned room. From exposed end of the intact 10-cm core segment of the core taken from 890 ft, a segment 1 to 2 cm thick had broken off during core recovery. This discolored and altered zone showed fractures roughly parallel to the exposed surface, passing through both paste and aggregates. This type of fracturing is characteristic of concrete damaged by cyclic phenomena, such as freezing and thawing or wetting and drying. Given that this concrete could not have been cyclically frozen, we attributed the damage to wet-dry cycles accompanied by precipitation of salts which kept the cracks open and permitted further damage.

42. The 812 and 890 core segments we studied represented only the first 15 to 18 cm from the inner surface into the shaft liner or key that is between 50 and 120 cm thick. Areas of intact concrete had approximately the phase composition, microstructure, and overall color and appearance of "normal"

portland cement concretes in good condition. Coarse aggregates were rounded particles of natural gravel, composed of the minerals dolomite and calcite. The aggregates, too, appeared "normal" in the bulk of each core.

43. Areas that appeared to the WIPP site staff to be deteriorated were, in fact, deteriorated. There were two distinct zones of discoloration on the affected end of each core segment: an outer, reddish-brown layer that was easily broken and had aggregates standing out where paste has been depleted and another layer that was a much darker gray than was the intact concrete but had not suffered as much loss of strength or mass. We confirmed that both discolored zones were reversibly hygroscopic when cycled between dry heat and lab conditions. This condition was attributed to the presence of hygroscopic salts of magnesium.

44. The aggregates were subrounded rock particles predominated by the mineral dolomite ($CaMg[CO_3]_2$). When observed by SEM, aggregates at the deteriorated ends of each core had surface features similar to those of comparable aggregates after mild acid etching. We considered the possibility of dissolution of paste and lesser dissolution of aggregate surface by weak acids formed by atmospheric CO_2 and groundwater. There is a strong positive airflow in WIPP shafts because of the mechanics of ventilating the repository rooms, and this would have provided an infinite supply of CO_2. Also, apparent salt deposits could be attributed to rapid evaporation of whatever groundwater reached the inner perimeter of the liner.

45. The deteriorated paste from the ends of cores 812- and 890-265 included calcium chloroaluminate as a major phase. As described in Section III, this phase forms readily in portland cement systems in environments with some alumina and abundant chloride. No chloroaluminate was detected in the deteriorated concrete from 812-340. Gypsum, brucite, sylvite, and halite were present locally.

46. As mentioned previously, grab samples were different enough from the concrete that we could not assume that they were related to the concrete from which they were removed. Grouts or mortars may have been applied to the inner surface of the liner or key during post-construction operations to control brine ingress or repair surficial damage. We did not consider the grab samples to be important in interpreting likely mechanisms of deterioration. However, it is significant that one of these samples (812-265) included

magnesium hydroxychloride hydrate. This crystalline phase is abundantly associated with joint-fill material at 834 ft, discussed in Sections III and V.

Conclusions and New Hypotheses

47. Our analyses of this first group of samples caused us to conclude that the surface of the liner and key was being altered by interaction between the portland cement and chemical agents available on this surface. As stated previously, we were unable to differentiate among at least three possible mechanisms of deterioration after this initial study. These were: direct interaction with brine, causing phase changes and resultant cracking and softening of the paste; physical effects of cycles of wetting and drying; and acid attack, the acid being provided by CO_2 that may be in abundant supply due to ventilation air flow in the shaft. Deterioration by biological activity also was possible on this surface.

48. The picture was further complicated by the probable presence of surface grout of unknown original components and brine of an apparently unnatural composition. Study of additional cores could not sort out all of these variables. However, we expected that studies of cores from an area of abundant brine but unaffected by CO_2 or cyclic wetting and drying could help us isolate the effects of the postulated chemical attack by brine. The cores taken from the 834-ft cold joint represent this condition. Their analysis is summarized in the next section.

49. Given all these possibilities and that samples represented locations where all of these mechanisms could have interplayed, WES and SNL recommended that cores should be recovered from along the cold joint at 834 ft. Concrete along the joint would not have been exposed to ventilation air that could have altered the degradation process (WES memo to SNL, 29 June 1990, Appendix B).

50. Details of laboratory methods, sample selection and preparation, and petrographic and other observations of each subsample studied are given in Appendix C of this report.

PART V: ANALYSES OF CORES FROM THE 834 COLD JOINT

Sampling and Analytical Techniques

51. Cores studied at WES during August and September 1990 were air-drilled at 834 ft, along a joint between two lifts of concrete that was at the junction between the shaft liner and basal key (see Figure 1). Each core was oriented such that it included the joint-fill material more or less along its long axis and the attached portions of the lifts immediately above and below the joint. The two core segments received at WES had field labels 834-1 and 834-2 and were assigned CTD numbers WIPP-2 DC-4 and WIPP-2 DC-5, respectively. Each were about 15 cm long with one end having been exposed in the shaft opening. Table 2 lists these cores. Core 834-1 was drilled to the west (about 270). Core 834-2 was drilled to the southwest. A third core from this depth, 834-3, was drilled to the north. This core was studied at Lankard Materials Laboratory (Lankard 1990).

52. These cores showed obvious alteration and deterioration along the cold joint and in the concrete lifts above and below. Each lift was further divided by bands of both "normal"-looking and reddish discolored concrete, in between which were several different layers of the joint fill materials (Figures 2 and 3). The joint apparently had been an open gap for an unknown length of time. With the information provided to us by SNL and WC/WIPP, we were unable to determine the exact history of materials used and sequence of injection or emplacement into this joint. Figure 2 is a photograph of one of these cores. The bend visible in Figures 2 and 5 along the joint is attributed to an offset in the joint as shown in Figure 1.

53. The two cores were subjected to extensive subsampling to separate visibly different layers and crystalline deposits. Our analytical work again centered around studying the phase composition and microstructure of each layer, its aggregate, and other distinctly identifiable components of the concrete and joint-fill system. Subsamples for individual study included: deteriorated and "good" cement paste; deteriorated and "good" aggregates; crystalline deposits from aggregate surfaces, fractures, and various layers of the joint-fill material; and the obviously different types of grouts along the joint. We used infrared spectroscopy to characterize the chemical grout among

the joint-fill layers. SEM, EDX, XRD, and petrographic techniques were used intensively on other materials.

Deterioration of Cement Paste

54. The deteriorated layers were almost exactly parallel to the joint and thicker in the lift below the joint (up to 50 mm thick vs. 20 mm or less for the upper concrete). The shaft-opening end of each core segment also was discolored and apparently deteriorated, which was taken to indicate deterioration by interaction between moving brine and concrete components. Both cement paste and aggregates were affected, indicating multiple mechanisms of degradation. The greater thickness and severity of damage below the joint was attributed to a difference in the original concrete; or a simple effect of gravity causing the brine to penetrate the concrete more, downward; or both.

55. Macroscopically demonstrable evidence for alteration and deterioration of the paste portion of the concrete in both lifts included: the existence of visibly different, reddish, discolored zones adjacent to the joint; softness of the paste (it could be easily removed by scraping with hand tools); and extensive fracturing and microfracturing, again roughly parallel to the joint, cutting through both paste and aggregate. The fractures were filled by apparent in situ crystallization of two phases. These were gypsum (hydrated calcium sulfate, $CaSO_4 \cdot 2H_2O$) and a complicated but well crystallized phase we had not previously encountered and for which we found no name: magnesium chloride hydroxide hydrate, $Mg_2(OH)_3Cl \cdot 3H_2O$ (JCPDS Powder Diffraction File pattern No. 7-412). The minerals brucite (magnesium hydroxide) and tetracalcium aluminate dichloride-10-hydrate (also called chloroaluminate) also were present. Reference X-ray powder diffraction data for phases identified in crystalline deposits and deteriorated concrete are in Appendix D.

56. Phase compositional evidence for deterioration of the paste portion of the concrete included: absence of calcium hydroxide and calcium silicate hydrates; and presence of magnesium chloride hydroxide hydrate, brucite (magnesium hydroxide), and gypsum where cement-paste phases should be. The apparently "good" concrete has the expected calcium hydroxide and calcium silicate hydrate. Calcium chloroaluminate is virtually absent from both good and deteriorated concrete above the joint at 834. It is present below the joint in

deteriorated concrete. It was present in the 812 deteriorated concrete, previously discussed, and absent from 890. As was mentioned in Section III, chloroaluminate can form only where both alumina and chloride are present in reactive forms. Even in a system that includes abundant sulfate, chloroaluminate may form in preference to ettringite if chloride is abundant. Availability of chloride should have been the same in the upper and lower lifts, assuming that the brine was the only source of chloride. This assumption is supported by EDX analysis of the cl distribution across the core taken at 834 ft (Appendix E). The absence of chloroaluminate in the lift above the joint suggests that there may not have been enough alumina for it to form. EDX analysis indicates that the total Al content of the intact concrete above the joint (layer Z) is lower than the Al content of the intact concrete below the joint (layer T). This leads us to speculate that the cement itself may have been different in these two concretes.

57. An even more plausible source of difference in total alumina would be a difference in fly ash used as a cementitious material in these two concretes. Analysis of EDX data accumulated from subsamples above and below the joint showed a difference in ratio of Ca to Si, giving more evidence for a difference in chemical composition of the cementitious materials. Considering that a time of several weeks elapsed between placement of concrete in the lift above this joint and concrete placement below, a change in materials is a strong possibility, even if they came from the same supplier. This possibly higher alumina content may have made the lower concrete slightly more susceptible to chemical attack and may have contributed to its thicker zone of deterioration. Given that we do not know whether of not the cement or fly ash was changed, all of this is speculation. But it may be important to consider the hypothesis that a subtle change in materials could make a notable difference to the potential for long-term durability.

58. EDX analysis of the deteriorated paste, both above and below the joint (Y and U, Figure 2), is deficient in the elements that comprise the bulk of portland cement (Ca, Si, Al, Fe) when compared to the undeteriorated layers (Z and T, Figure 3). Most of this difference is caused by Ca depletion in the deteriorated layers.

Deterioration of the Aggregates

59. On the shaft-opening end of each core, aggregates stood out in relief where the deteriorated paste had lost mass. The dolomite coarse aggregates in the lower deteriorated concrete were coated with white crystalline material. It was present but less abundant around aggregates immediately above the joint. XRD analyses proved these coatings to be largely magnesium chloride hydroxide hydrate, accompanied in the lower lift with brucite and gypsum. This lower deteriorated zone (U on Figure 2) is fractured throughout, its fractures running roughly parallel to the joint through paste and aggregates without differentiation. Fractures, too are infilled with the same suite of white crystalline minerals, which are present also in voids in the paste and in aggregate pores. This layer was easily broken (if a sample was dropped onto a table, for example) into thin parallel bands along these mineral-filled fractures, again without differentiating paste and aggregate.

60. Individual coarse aggregates straddled the boundary between discolored and "good" concrete (between U and T on Figure 2). These aggregates tended to break along this boundary when probed with a dental pick, rather than break out of the paste. In fact, each individual aggregate broke along the line where the discoloration stopped, and fractured into many parallel pieces above this interface (the portion that was within U). That portion of each aggregate that was within the "good" paste (T) remained intact and bonded to the paste. Recall that this boundary is not from casting, but is apparently a front representing the extent of chemical alteration. Their fracturing showed that the aggregates, too, were softened by chemical attack.

61. Although physical alteration to the aggregate in the deteriorated layers was conspicuous, there was little change in the chemistry as revealed by EDX analysis (Appendix E). The only statistically significant change was in the Ca and Si levels in comparisons of aggregates in the U and T layers. Silicon is a minor component of the aggregate and the change in Ca is small relative to the total Ca present, so the importance of these changes, if any, is unknown.

62. During scoping studies WES demonstrated that similar dolomite aggregates were affected by contact with a sample of brine from the collector ring. For this experiment, we obtained a similar dolomite aggregate from a

Carlsbad, NM, supplier, and soaked individual particles in brine from the collector ring for a few days. Surface condition of each aggregate particle was documented by SEM before and after treatment. Samples of the same aggregate also were soaked in a dilute acid solution. The appearance of the surfaces of aggregates had changed similarly after both treatments. WES recommend study of the effect of the complex WIPP brines on various aggregate types, to determine the aggregate type with the best promise of durability in this environment.

Joint-Fill Materials

63. A chemical grout, with an open cellular structure and rubbery texture, was present in both cores, between crystalline layers along the joint. (All of these layers are part of W on Figures 2 and 3. We had not yet differentiated the various joint-fill materials when we assigned letters.) This rubbery grout layer was thinner toward the shaft-opening end of each core and thickened roughly from 2 to 6 mm toward their broken ends (toward the host rock). It was thickest just before the down-angle of the lift surface key. Both cores appeared to have had a gap at this angle, partly infilled by the chemical grout and crystalline layers, but still partly open. Behind the gap, the chemical grout layer thinned and stopped. The chemical grout was identified by infrared spectroscopy as an acrylate.

64. The open cells of the rubbery grout were partly infilled with a maze of lath-shaped, clear crystals of gypsum (identified petrographically and by XRD). The crystalline layers above and below this grout, each a millimetre or less in thickness, were magnesium chloride hydroxide hydrate and brucite. Some of these thin deposits were discontinuous, but at least four of them were distinguishable by alternating red and white color. Their appearance suggested several cycles of brine flow and crystallization, from which we inferred the possibility of an inconstant supply of brine. It is also plausible that the chemical grout acted as a semipermeable membrane, allowing calcium sulfate to crystallize cleanly within its open cells but excluding other ions, which in turn formed the adjacent red and white layers. There are other possible explanations.

65. The grout layer below the chemical grout is an enigma. It appears to be a sanded cement-based grout. Yet it has no phases associated with portland cements. It is unusually high in magnesium and chloride and low in calcium and silica (EDX analysis, Appendix E). If this grout had originally been portland-cement based, apparently it was chemically altered to something entirely different. As was discussed in Section III, it is possible that this was originally a sorel cement, thus accounting for its unusual phase composition. If sorel cement was used here or between the concrete liner and the host rock, it may have contributed magnesium to the brine and may have enhanced the unwanted chemical assemblage that caused magnesium hydroxide chloride hydrates to crystallize in voids and fractures.

Conclusions and Recommendations

66. Our observations of the cores drilled along the cold joint led us to the following conclusions and recommendations. First, the deterioration we saw was most likely attributable to chemical interaction between magnesium-bearing groundwater and the shaft-liner concrete. Second, these interactions were both chemical and physical, but the physical deterioration was directly related to chemical interactions of magnesium and various sulfates with the phases of portland cement, pozzolans, and aggregates of the original concrete. The roles of CO_2 and cyclic wetting and drying in the deterioration probably were minor because concrete along the joint was not exposed to flowing air in the shaft.

67. It appeared that chemically active brine had access to the concrete liner and its inner circumference through the cold joint. From this, we inferred that brine reached the joint by flowing along the interface between liner and host rock, if only for a short distance. This inference led WES and SNL to consider that the concrete also might be deteriorating along the interface. Therefore, WES and SNL recommended that cores be drilled and recovered from the full thickness of the shaft liner and through to the host rock, from within a meter both above and below the cold joint. We predicted that the condition of the concrete at this interface would indicate whether or not the deterioration mechanisms were at work on the concrete at the annulus of the shaft. Further, if we found evidence of deterioration there, the thickness of

the deteriorated layer could be a basis from which to approximate the deterioration rate. This added a third phase to our study of the waste-shaft liner concrete, as described in the next section.

68. Our initial conclusions about deterioration mechanisms, based largely on evidence from XRD and SEM of subsamples from these cores, were provided to SNL in an informal memo on 15 September 1990, slightly revised on 18 September 1990. The second version is included in Appendix B.

PART VI: ANALYSES OF CORES ABOVE AND BELOW THE 834 JOINT

Why These Cores Were Studied

69. All of the chemical changes and resultant loss of strength of the concrete along this joint were attributed to chemical interaction between brine and concrete or grout. This brine had to be flowing along the cold joint for this to occur. It was logical to assume that brine was also moving along the interface between concrete liner and host rock. This led us and SNL staff to hypothesize that the concrete may also have deteriorated along its interface with the rock. Sandia and WES recommended that cores be drilled through the liner and into the rock behind it, and that WES should determine if these cores showed the same type of deterioration observed on the others. This drilling was accomplished at 832 and 836 ft by WIPP Site staff late in October 1990. WES received the cores on 2 November 1990. Sample identification is in Table 3.

Analysis and Results

70. The 832 and 836 cores were analyzed at WES by the same techniques applied to the cores described previously, particularly petrographic study and phase composition by XRD. Having reason to believe that the lifts might have had different cements or pozzolans, we compared other obvious concrete characteristics, especially parameters of the air-void systems, and aggregate types and sizes. Air-void systems were not notably different, and aggregates were mineralogically similar. However, the maximum aggregate size of the upper lift (832) was 0.75 in., while that of the lower lift (836) was 1.75 in.

71. The core segments from the "back" of each drillhole, including concrete from the annular interface, were cut in half along their long axes for observations of fresh surfaces of the concrete. One half of each was archived.

72. Deterioration was apparent at the end that had been closest to the host rock. Deterioration was more extensive at 836 ft, below the joint, where the thickness of obviously altered concrete was about 45 mm. Above the joint, at 832, the deterioration extended about 30 mm into the core from the rock

interface. Evidence of deterioration was the same as that seen along the joint at 834 ft: discoloration and softening of the paste; fractures through the paste and through and around aggregates; crystalline magnesium hydroxide and hydroxychloride hydrate as rims around aggregate particles and in voids in the paste; and the phase assemblage of the paste, which included chloroaluminate and magnesium compounds. Away from this deteriorated zone, the concrete was intact and in apparently excellent condition.

73. One sample received at WES had been identified in the field as representing the host rock behind the liner. This sample was not obviously "rock." It was analyzed by techniques used to isolate and differentiate clay minerals (Carroll 1970). This apparently clay rock was found to include the clay minerals chlorite, clay-mica (illite), and kaolinite, accompanied by quartz, feldspars, micas, magnesite (magnesium carbonate), and halite, plus some traces of other non-clay minerals. Of the two core segments that might have been bonded to rock behind the concrete liner, neither showed any evidence that it had been. If this clay-rock represents the host rock at this depth, concrete would not have bonded easily to it.

PART VII: CONCLUSIONS

74. The concrete of the WIPP waste shaft liner has been affected by chemical interaction with high-magnesium brine. The result of this interaction is deterioration of the concrete at those locations where it is in direct contact with the brine. These contact areas include at least some portion of the interface between concrete and rock, at least some of the cold joints between concrete lifts, and the vertical circumference of the shaft opening.

75. The deterioration mechanism is not simple. The cementitious and strength-giving phases of the paste portion of concrete have been altered to compounds that impart no strength. Aggregates also have been fractured and softened along with the paste surrounding them. Crystalline deposits of magnesium-bearing minerals and gypsum filled the fractures and assured that they would remain available flow paths for brine.

76. There is physical evidence along the cold joint that one or more materials were injected to stop groundwater movement either along the joint or at the concrete/rock interface. The deterioration of the concrete along this joint and at the interface indicates that this attempt was not effective, and that magnesium-bearing groundwater remained available for chemical interaction.

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Table 1

Identification of Shaft-Liner Samples Received at WES During June 1990 for Scoping Studies

Field ID	SL Serial No.	Description
812-340	WIPP-2 DC-1	Concrete core, 7-cm diam; 14 cm long
812-265	WIPP-2 DC-2	Concrete core, 7-cm diam; 16 cm long
890-265	WIPP-2 DC-3	Concrete core, 10-cm diam; 11 cm long
812-145	WIPP-2 SM-4	136 g of granular material
812-265	WIPP-2 SM-5	114 g of granular material
890-085	WIPP-2 SM-6	128 g of granular material
0002	WIPP-2 SM-7	230 ml of liquid, with sediment

Table 2

Identification of Shaft-Liner Cores Received at WES during August 1990

Field ID	SL Serial No.	Description
834-1	WIPP-2 DC-4	Core segment 7-cm diam; 14 cm long, along interface between two concrete lifts
834-2	WIPP-2 DC-5	Core segment 7-cm diam; 15 cm long, along interface

Table 3

Identification of Shaft-Liner Samples Received at WES during November 1990

Field ID	SL Serial No.	Description
836-1/3	WIPP-3 DC-1	Concrete core, 10-cm diam, 17 cm long, has pilot hole
836-1/4	WIPP-3 DC-2	Concrete core, 10-cm diam, 15 cm long, has pilot hole
836-1/5	WIPP-3 DC-3	Concrete core, 10-cm diam, 14 cm long, pilot hole, clay on both ends
832-1/3	WIPP-3 DC-4	Concrete core, 10-cm diam, 24 cm long, pilot hole
832-	WIPP-3 SM-1	Several grams of dark clay
832-	WIPP-3 SM-2	Apparent clay from end of DC-4

Table 4

Phase Composition of Components of Cores 834-1 and 834-2, Identified by XRD

Layer (from Fig. 2)	Phase Composition
Z - good concrete, above joint	calcium silicate hydrate calcium hydroxide calcium hemicarboaluminate calcium chloroaluminate (trace)
Y - partially deteriorated, above joint	calcium chloroaluminate calcite dolomite
X - top of joint fill	organic
W - with chemical grout in joint	gypsum brucite calcite magnesium hydroxide chloride hydrate
V - grout in joint	gypsum magnesium hydroxide chloride hydrate brucite magnesium silicate hydrate
U - deteriorated concrete below joint	gypsum magnesium hydroxide chloride hydrate ettringite halite (on surface) calcium chloroaluminate
T - concrete below joint	calcium silicate hydrate calcium hydroxide calcium hemicarboaluminate ettringite calcium chloroaluminate

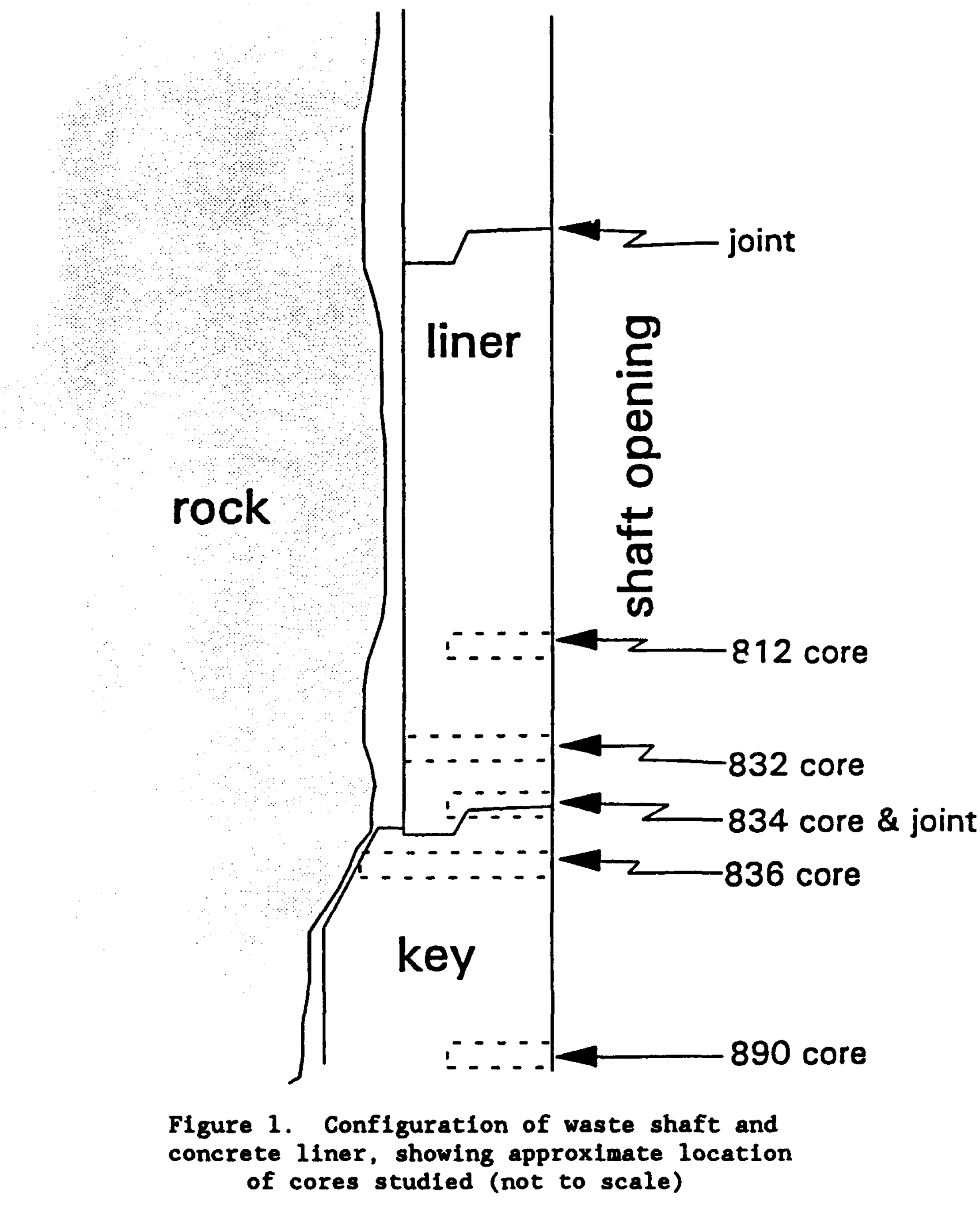
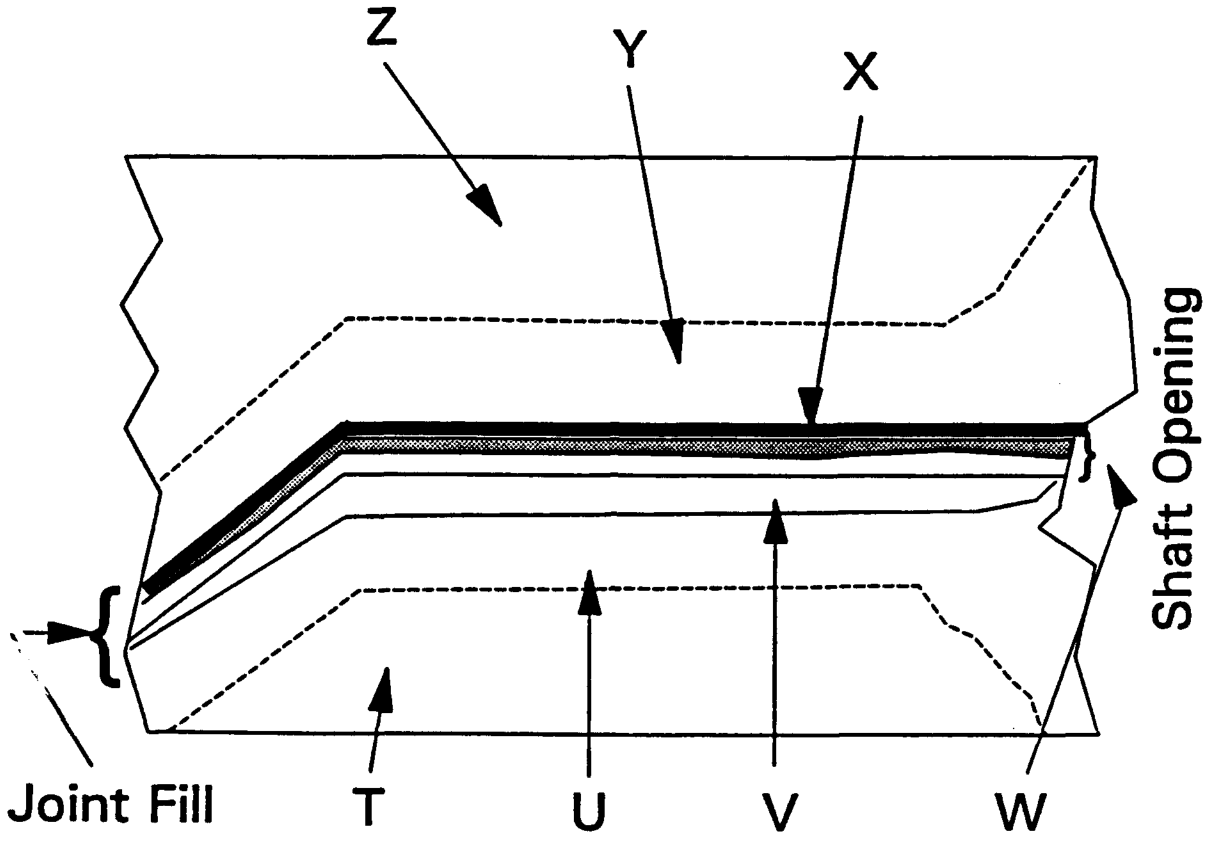
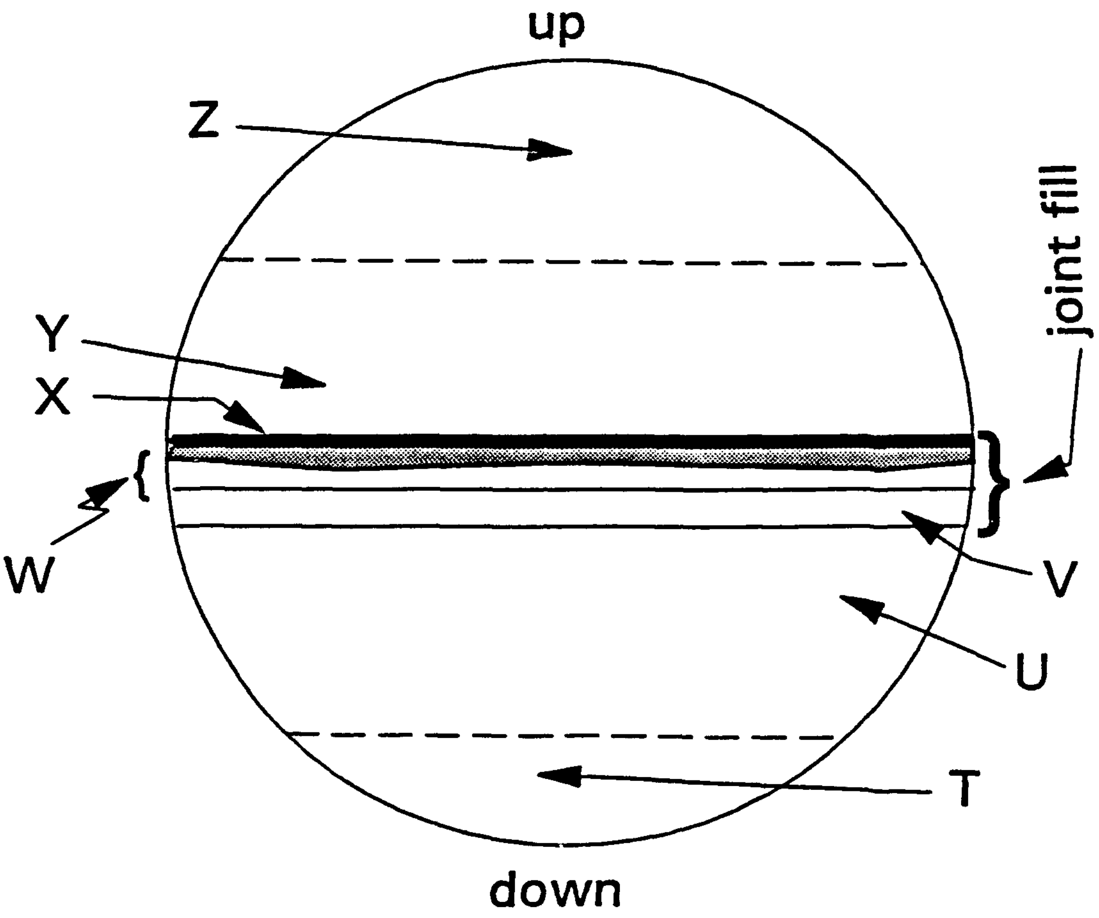


Figure 1. Configuration of waste shaft and concrete liner, showing approximate location of cores studied (not to scale)



Z, sound concrete
Y, partially deteriorated concrete
X, black material (local)
W, chemical grout + crystalline material
V, sanded grout
U, deteriorated concrete
T, sound concrete

Figure 2. Lateral view of external features of 834-1 and 834-2. Cores are approximately 15 cm long



Z, sound concrete

Y, partially deteriorated concrete

X, black material (local)

W, chemical grout + crystalline material

V, sanded grout

U, partially deteriorated concrete

T, sound concrete

Figure 3. Cross section of 834-1 and 834-2. Cores are 7.5 cm across

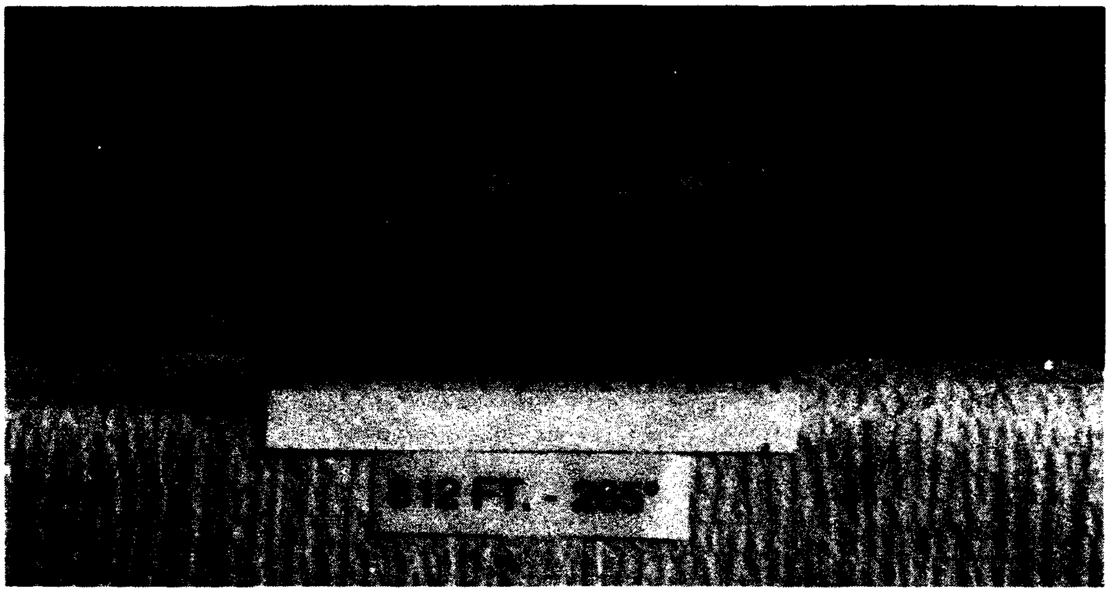


Figure 4. Core segment from 812-265

Figure 5. Core segment from 834, viewed on surface cut perpendicular to long axis

APPENDIX A: SPECIFICATIONS FOR THE SHAFT-LINER CONCRETE

Concrete Materials and Proportions

Specifications for concrete materials and mix proportions were prepared by the US Army Corps of Engineers, Albuquerque District, reference "Invitation for Bids, DACW 47-83-B-0010, Specifications for Construction Contract Package 1FB/ID, Underground Experimental Areas/Waste Shaft and Exhaust Shaft at Waste Isolation Pilot Plant, Carlsbad, New Mexico," dated 1 April 1983. Analyses of cement and pozzolan and other information about mixture proportioning were communicated from Dr. J. Nowak to Dr. L. D. Wakeley by telephone and FAX on 18 September 1990. This information is summarized below.

Cement. Cement was specified to be ASTM C 150, Type V and to be from a single source. A mill certificate for cement delivered from Southwestern Cement Company, Odessa, TX, contained the following information, which complies with the specification.

SiO_2	22.62
Al_2O_3	3.13
Fe_2O_3	5.44
CaO	65.16
MgO	0.70
SO_3	1.94
LOI	1.90
Insol Res.	<0.75
C_3S	59.0
C_2S	20.3
C_3A	0.0
C_4AF	16.5
Alkalies, as Na_2O	0.24
Blaine fineness	393 m^2/kg

Wagner fineness	219 m^2/kg
3-day strength	2730 psi
7-day strength	3890 psi
Air content	9.5%

Pozzolan. Pozzolan was specified to comply with ASTM C 618, except that loss on ignition was specified to be less than or equal to 6.0%. Class C fly ash (ASTM C 618) was supplied from Panhandle Ash, Harrington Station, Amarillo, TX. A mill certificate contained the following information, which complies with the specification.

SiO_2	42.1%
Al_2O_3	16.0%
Fe_2O_3	5.6%
SO_3	1.42%
CaO	25.0%
MgO	4.6%
Moisture	0.05%
Loss on Ignition	0.21%
Na_2O	0.7
K_2O	0.3
Pozzolanic Activity w/Lime, 7 days	1920 psi
Pozzolanic Activity w/Cement, 28 days	105% of control
Water Requirement	89% of control
Increase in Drying Shrinkage	0.0063% at 28 days
Specific Gravity	2.65
Fineness, % Retained 45μ Sieve	16.52%
Soundness, Autoclave	0.127%

Aggregate. Locally available river-run aggregates were used. At least three sizes of coarse aggregate were used during the construction. These were

0.75 in. max, 1 in. max, and 1.5 in. max. No other petrographic information was available.

Admixtures. High-range water reducer, Type F, from Master Builders, was used. No NaCl or $CaCl_2$ was believed to be used.

Water. Water was taken from the Carlsbad city water system.

Other. Concrete was supplied by Southeast Ready Mix.

Concrete Mix Design. Descriptions, or partial descriptions, of at least two concrete mixture designs were found in the construction documentation, as described in columns 2 and 3 below. Information from one batch ticket is summarized in column 4 below.

Ingredient	Design 1	Design 2	Batch Ticket
Cement	508 lb/yd^3	540 lb/yd^3	550 lb/yd^3
Fly Ash	56 lb/yd^3	118 lb/yd^3	-
Water	29 gal/yd^3 (281.7 lb/yd^3)	31 gal/yd^3 (258 lb/yd^3)	28.5 gal/yd^3
Coarse Aggregate, 1.5 in*	1,947 lb/yd^3	1,900 lb/yd^3	1,736 lb/yd^3
Fine Aggregate*	1,278 lb/yd^3	1,344 lb/yd^3	1,417 lb/yd^3
Pozzolith	68 oz/yd^3 (400N)	24 oz/yd^3 (300N)	73 oz/yd^3
MBAE-10, MBVR	17 oz/yd^3		9 oz/yd^3
Entrained Air	4%		

* At least one batch ticket indicated substitution of 860 lb of 3/4 in., 860 lb of 1 in., and 1,403 lb of fine aggregate.

APPENDIX B: MEMOS EXCHANGED BY SANDIA NATIONAL LABORATORIES (SNL) AND US ARMY ENGINEER WATERWAYS EXPERIMENT STATION (WES), CONCRETE TECHNOLOGY DIVISION (CTD) DURING THIS PROJECT

18 Sep 90
CEWES-SC
L. D. Wakeley

Unofficial Summary of Analyses in Progress, Concrete Cores from WIPP Waste Shaft

INTRODUCTION

1. This draft report summarizes what we have determined from our analyses, of cores taken from the Waste Shaft at the Waste Isolation Pilot Plant (WIPP) and studied during the period 10 June through 11 September 1990. This report is unofficial (has not been through WES review). It includes conclusions, interpretations, and recommendations, without full explanation of the analyses performed or the full range of evidence for each conclusion. It has no descriptions of lab procedures. The entire range of work performed during these analyses will be presented in a WES report to be published during FY 91.

WASTE SHAFT CORES

2. In this discussion, the ends and faces of cores and core segments will be described as S -- the end toward the shaft; or R -- the end toward the rock.

3. The cores we studied beginning in June were from 812- and 890-ft depth, with 890 being 4 in. below a horizon of water entry into the shaft. Each of these showed deterioration on the S end. Additional "grab" samples from these depths also showed obvious and extensive deterioration, with virtually no apparent cement paste. Aggregates stood out in relief on each S surface, and loose aggregates were present in grab samples. The coarse aggregates were dolomite and calcite, accompanied by sand of the sane minerals plus quartz. The top of the Salado Formation is at approximately 810.

4. After studying the 812 and 890 materials, I had recommended that we needed to see material taken along a joint, from where groundwater appeared to be flowing into the shaft. The purpose was to define better the causes of deterioration. It had seemed plausible, after seeing the S ends of the 812 and 890 cores, that the concrete might have suffered from acid attack, the acid source being related to the abundance of CO_2 available via strong positive air flow up the shaft. Cores taken from along a leaking joint should show deterioration, if any, unrelated to the air flow.

5. Cores studied during August and September were air-drilled at 834 ft, along a joint between two lifts of concrete. 834-1 was drilled to the west, about 15 cm long. 834-2 was drilled to the southwest, and is about 14 cm. A third core from this depth, 834-3, was drilled to the north and is being

analyzed by Dave Lankard. 834-2 is the wettest hole (RE/SPEC), and 834-3 the driest.

6. The following paragraphs list what we (think we) know, from physical inspection of cores and slabs through various ranges of magnification and by extensive XRD work. The second report (attached) gives more of what we know, principally by analysis of data from EDX. Both reports give related hypotheses and suggestions for other research.

WHAT WE KNOW

7. Deterioration of Cement Paste. The cement paste fraction of the concrete has deteriorated by interaction with water, everywhere it was in contact with water. At 834, this is along the entire length of the core parallel to the joint, both above and below the joint, thicker below. The S surface also is deteriorated. Symptoms at 834 are: softening of what should be the cement paste fraction of concrete; absence of calcium hydroxide (CH) and calcium silicate hydrates (CSH); presence of parallel microfractures across the concrete parallel to the joint, filled with magnesium chloride hydroxide hydrate (MClH) and gypsum; discoloration in zones above and below the joint, more pronounced below; and presence of MClH, brucite (MH), and gypsum where hydrated cement paste should be. Aggregates stand out in relief on S, where the paste appears to have been removed.

8. Symptoms at 812-S are: softening, discoloration, aggregates in relief, absence of CH and CSH, presence of gypsum, brucite, ettringite (6-calcium aluminate trisulfate-32-hydrate), and tetracalcium aluminate dichloride-10-hydrate a.k.a chloroaluminate. This last phase is abundant in grab samples and surface materials from 812. EDX analyses show an unusually high Fe content in the chloroaluminate. This plus the high percentage of C4AF reported for the cement suggests the possibility that chloroaluminate might form from C4AF, even from a zero-C3A cement. 890 showed less deterioration. There was no chloroaluminate or ettringite in the deteriorated material at 890. All surface samples have NaCl. Some have KCl.

9. Special Note About Cement, and this is important. Chloroaluminate is virtually absent in both good and deteriorated concrete above the joint at 834. It is present below the joint (we are still working on it), where deterioration is more extensive. Ettringite is absent at 834 above the joint, and present below. Chloroaluminate is abundant in the surface mess from 812, and ettringite is present in intact concrete at 812. These phases are absent from deteriorated material at 890.

10. Chloroaluminate and ettringite can form only when there is aluminum present and available. This implies strongly that there is Al present and available in the concrete used at 812 and below the joint at 834, but not present or available in the concrete immediately above the joint at 834 or at 890. This may mean that the cements or fly ashes used for concrete in different lifts had slightly different Al contents. This may also mean that it is critical to have virtually no Al available, as the concrete above the joint at 834 shows very little deterioration. Poole's analyses of EDX data (attached) has evidence of a difference in Ca/Si ratio above and below the

joint, which also supports the hypothesis that different cements were used. The more extensive deterioration below the joint indicates that this subject needs more work, fast. (The analysis of cement provided by Nowak shows 0% C3A, but over 16% C4AF, and 16% Al_2O_3 in the fly ash (which also had 25% CaO). We still have not actually seen any fly ash.)

11. Figure 1 is a generalized view of core 834-2 along its axis. Most of our mineralogic analyses were performed on slabs or disks cut from 834-2. Figure 2 shows the face of slab 4 of 834-2. I will use the letter designations given on those figures to discuss the layers and differences among them. The individual layers become more obvious as the discs dry. After several days in the open, Y appeared very little different than Z, but U showed up as totally distinct in color and character. V, where present, became so obvious that I cannot believe I missed it earlier (see para. 18).

12. Deterioration of Dolomite Aggregate. The dolomite coarse aggregate in U, and to a lesser extent in Y, is coated with white crystalline material, which diminishes the bond to paste. This material is largely MClH, accompanied in U with brucite and gypsum. The U layer is fractured in many layers parallel to the joint, which run through paste and aggregate almost undifferentiated. The layer was still intact, even through slabbing with a fairly large saw.

13. Each tiny fracture is recognizable by the white crystalline fracture fill, which is MClH and gypsum. When you try to break U (hit it), it breaks through the aggregates into thin parallel bands along these fractures. Larger aggregates break out along their white crystal coating. The most bizarre feature of the aggregate in U is its tendency to break along the interface between U and T. When probed individually (with a dental pick), aggregates along this interface broke along the line where deterioration stopped, and fractured into many parallel pieces (not parallel to the joint) above this interface in U, while that portion of an aggregate grain surrounded by paste in T remained intact and bonded to the paste.

14. We documented experimentally that the surface of dolomite aggregate is affected by the brine from the collector ring. We need to do more work on the nature of this dolomite/brine interaction. It is possible that dolomite aggregate is a poor choice in this environment. However, it appears to us that the aggregate fracturing is due to salt deposition (a physical mechanism) rather than to alkali-carbonate reaction (chemical degradation).

15. Evidence for Deterioration Related to Movement of Water Along Joint. The main evidence is the presence of U and Y layers parallel to the joint. This means the changes in the cement paste are not dependent on any mechanism related to air flow. As mentioned, the U layer is more distinctly deteriorated: it is thicker, has a color strikingly different than of the unaffected concrete Z, is shot full of crystal-filled fractures, and breaks more easily. See report on EDX data for more discussion of this.

16. The joint itself is infilled with crystalline material throughout, in parallel bands differentiated by differences in color visible at low-power magnification. These layers are gypsum, MClH, and brucite. The layers break apart into parallel planes, alternating reddish and white. This suggests

nonuniform or nonconstant flow or availability of water, resulting in multiple episodes of crystallization.

17. Grout Layers are Present but Discontinuous. A chemical grout, with an open structure and rubbery texture, is present (W) in both 834-1 and -2, immediately above the crystalline layers (all of this is in W -- we had not differentiated them yet when we assigned letters). This rubbery grout layer is thinner toward S and thickens (roughly 2 to 6 mm) toward R, reaching its thickest point just before the angle-down of the lift surface. Both cores show an apparent gap at this angle, partly infilled by chemgrout and crystal layers, but still partly open. Where the lift surface angles at 45°, the chemgrout layer thins out to nearly nothing. The open structure of this rubbery white layer is partially infilled with clear gypsum crystals (lath-shaped).

18. An apparent clay-grout is present in 834-2, 10 mm thick at R and up the lift-surface angle, about 7 mm, halfway along the core, and thinning to essentially absent at S. This layer is not obvious in 834-1, and if present is very thin. Its presence and distinct appearance becomes more obvious as the core dries (you should see the slab we put in the SEM!). V appears to have very little, if any, evidence of cement binder. It is distinctly soft, much softer than U, and fine grained. Its color is almost exactly that of U when they are wet, however, and even we missed it when we first looked (so nobody in the shaft noticed it, either). Its presence makes the deterioration of concrete below the joint look thicker than it is.

19. Surface Effects. NaCl is present exclusively on the S surface at 834, 812, and 890. This suggests that it only crystallizes out of the fluid where there is exposure to air, presumably where there is rapid evaporation. Evaporation also appears to be the cause of the buildup of hygroscopic salts in S deteriorated grab samples and surfaces. These salts keep the surface wetter, by grabbing any available moisture from the air.

20. Strong Concrete. A core from 812 was tested for compressive strength. It was over 9,000 psi. One value does not mean much, but it certainly says that where this concrete looks to be in good condition, it probably is. The deterioration is not global. Even at 834, the Z layer was hard enough that it was difficult to separate a powdered sample for XRD (that is, it required the kind of effort we are accustomed to for "good" concrete). CSH and CH are present in intact concrete, as expected.

21. The Black Layer and Other Grout Questions. There is a black layer, X on Figure 1, which is really only obvious on R of both cores. It is carbon by EDX and flames off as an organic when tested, leaving an unremarkable elemental assemblage. According to Dr. Nowak (13 Sep), pressed bentonite sheets were used at the bottom of the form at this depth. These sheets had a black paper backing. This black-layer may be remnants of that form liner. Lankard told me (11 Sep 90) that he had learned from Westinghouse people that there were as many as four separate episodes of grouting, a year or more after concrete placement: 2 chemical and 2 cement (or clay/cement, is my guess). These cores show that these different grouts infilled this joint in different places. It would take evaluation of more cores from more joints to determine

if water movement along the 834 joint is related to the presence of any particular grout.

SUMMARY

22. The concrete has been affected by contact with the available groundwater. This deterioration is embodied by Mg phases in former cement paste, softening, and discoloration of concrete. Aggregates also are affected, as shown by crystalline coatings, and tendency to fracture at the interface between "bad" and "good" concrete. The deterioration is worse below the joint, by one or more of these mechanisms: 1) gravity, providing more of the reactive groundwater below the joint; 2) clay grout or other grout below the joint providing an additional zone of saturation and keeping the caustic fluid in direct contact with the concrete; 3) use of a different cement (and/or fly ash) in the concrete of the lower lift, that cement being one which is more susceptible to Mg attack. XRD and EDX data give evidence of the "different cement" scenario. Concrete at 812 is more like that below the joint at 834. Concrete at 890 is more like that above the joint at 834.

23. NaCl is only present at the exposed surface of concretes, where evaporation could occur.

24. The Ca and Cl levels in the fluid from the collector ring are higher than can be explained as the local groundwater. A plausible source of Ca is the cement paste, by exchange of Mg for Ca, giving us the softening and deterioration we have described. We have no direct evidence for removal of mass from the cement paste, but as of 18 Sep we are working on it. If $CaCl_2$ was used in the concrete (the consensus is that it was not) or in one or more of the grouts (somebody at Westinghouse told me it was), then I suggest much of this $CaCl_2$ came right out with the groundwater, to account for higher levels of both Ca and Cl. (We have an awful time trying to explain the Cl otherwise: if from NaCl, then where was all the Na? It is much neater and more plausible as available $CaCl_2$.)

25. We cannot know the effect of the various grouts on water movement and concrete deterioration without knowing much more about what grouts were pumped where, and without sampling from more joints.

WHAT TO DO NEXT

26. The worst-case scenario is this: Assuming that the groundwater coming out through the joints is flowing down from the rocks above, and assuming that its flow path takes it down the annulus between concrete and host rock, then we have the potential for much more concrete deterioration all along the interface between concrete and host rock. We would have to analyze cores drilled through the concrete and into the rock to determine this. It is certainly something that we need to know now, rather than 5 years from now.

27. The concrete used for the liner and below was not salt saturated. There could have been a wide gap at the annulus (the concrete water would have dissolved some of its host rock), providing free flow of water and requiring

several episodes of grout to try to close it up. Drilling through the contact should tell us how wide that space was, and how much of a flow path it provided.

28. We can design experiments to determine the extent to which Al content of cement and fly ash affects concrete deterioration in this environment. We could be talking about extremely minor differences in total chemical composition having an amazing impact on tendency to deteriorate. We need to know this for the Plugging and Sealing Program, and for all future concrete placements. Likewise, we can determine if dolomite aggregate is unsuitable, and need to do so a.s.a.p.

12 Sep 90
CEWES-SC-EM
Toy Poole

Unofficial Summary of Analysis in Progress of Concrete Cores from the WIPP Waste Shaft

EDX Analysis

Data

Four scans were taken across the surface of a cross-sectional disc of core WIPP-2 DC-5. Energy dispersive x-ray (EDX) analyses were made at various intervals on these transects, but generally every 2 to 4 mm. For purposes of statistical description of results, data were grouped in approximately 4 mm increments, except where there appeared to be a qualitative change in the concrete, as described in Figure B1. For this particular disc, these changes occurred as follows:

Z - layer of good concrete above lift interface, 0 - 10 mm
Y - layer of deteriorated concrete above interface, 11 - 21 mm
W - crystalline layer in interface, 22 - 25 mm
V - sanded grout layer below interface, 25 - 30 mm
U - layer of deteriorated concrete below interface, 31 - 52 mm
T - layer of good concrete below interface, >52 mm

The chemical composition of each 4 mm interval was represented by a mean that was derived from 3 to 8 local analyses.

Description of Chemical Gradients

Calcium (Ca) levels in the good concrete at the top and bottom were about as expected from normal portland cement, but there was a statistically distinct depression that corresponds to the sanded-grout and lower-deteriorated-concrete layers (20 - 50 mm). There was some depression in the upper-deteriorated layer, but not nearly to the extent of the lower layer. Ca content of the lower layers of good concrete is a little higher than in the upper layers of good concrete.

Silicon (Si) levels fluctuated in what appeared to be a random way across the surface of the slice, but statistical analysis indicated that these fluctuations were greater than our sampling error, thus probably indicating real differences. Si in the upper good concrete is slightly higher than levels in the lower good concrete.

Chloride (Cl) levels in the good concrete are consistent with some addition of $CaCl_2$ as an admixture. Levels are high in the deteriorated concrete above and below the interface and are very high in the sanded grout layer.

Magnesium (Mg) level s are low and variable, but as in the silicon analysis, variation is larger than sampling error. There is a particularly large peak corresponding to the lower deteriorated concrete layer (36 - 38 mm). In general, there appears to be more Mg in the lower concrete than in the upper concrete.

Potassium (K) appears in substantial quantities only in the sanded grout layer.

Sodium (Na) levels parallel Cl levels in the concrete above the interface, but are generally lower than expected from Cl contents in concrete below the interface.

Sulfur (S) is present in measurable quantities only in the chemical grout layer (23 mm).

General Interpretations and Recommendations

Ca and Si levels tend to some degree to parallel each other, suggesting that where Ca and Si are both high, there is abundant calcium-silicate-hydrate (CSH), and where they are both low, or one is low, that CSH has been destroyed and removed. Using this logic, the CSH content in the upper deteriorated concrete is only somewhat depressed relative to the good concrete. In the lower deteriorated concrete, the CSH content is severely depressed in that the Ca levels are very low near the lift interface and increase towards the good concrete below the interface. In this layer, however, both Si and Mg are higher than background levels, suggesting that Mg has substituted for Ca to make a non-cementitious magnesium-silicate-hydrate (MSH) phase. This is further supported by the relative constancy of the Ca + Mg (corrected for molecular weights) profile across this region of the core. These patterns suggest that the lower concrete has been severely deteriorated by the action of Mg salts and that some of the portland cement-derived reaction products have been leached out.

Ca-Si levels are severely depleted in the sanded grout layer, which appears to be mostly KCl.

The high sulfur content of the chemical grout layer was expected from the abundant gypsum crystals observed there.

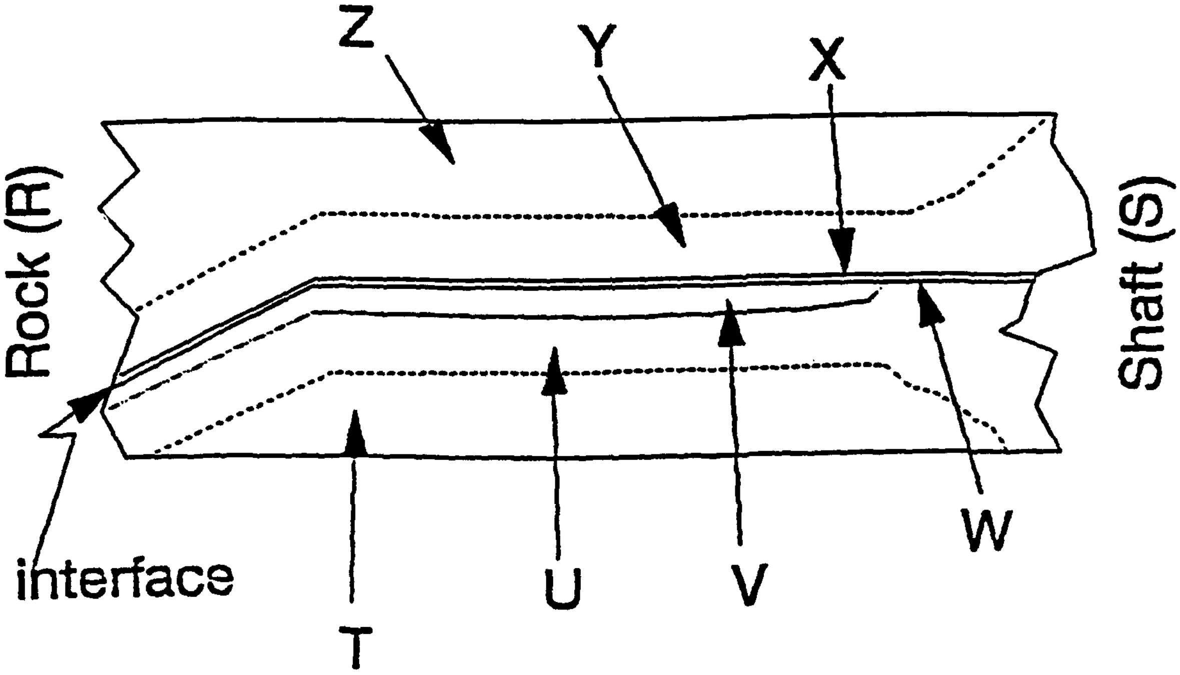
The concrete above the interface may be made from a different cement than the concrete below the interface. This is evidenced by the Ca-Si ratio of these two layers. The Ca-Si ratio of the good concrete above the interface is 4.7 while the same ratio in the good concrete below the interface is 6.9. However, an alternative explanation of this pattern is that the amounts of aggregate vary between the concretes. Such variation in aggregate content, which is high in Ca, could give the same pattern because the EDX analyses were not necessarily of paste only, but were of random spots in the concrete. The extent of sampling is not extensive enough to really verify this from this type of analysis.

It should be noted that EDX analyses give data on the relative composition of the substance under examination, but do not give data on total amount of that substance per cubic centimetre of concrete. For example, if the CSH has deteriorated and has been removed from the concrete, EDX analysis does not give us direct evidence of this removal of a certain mass of the material, but only gives us indirect evidence from changes in relative composition of whatever material is under examination. Physical loss of material can be measured and probably should be measured.

That the concrete below the lift interface is more deteriorated than that above the interface may be due to differences in materials or it may be due to differences in groundwater flow, assuming that the ground water is the principal degrading agent. If the concrete is relatively permeable, then gravity-forced flow of ground water from the lift interface would result in more deleterious reactants getting into the concrete. Movement of ground water into the concrete above the lift interface would depend more on capillary forces, and might therefore be of lower volume.

The ground water believed to be present in this area is quite high in Mg. Mg is known to be quite deleterious to hydrated portland cement under certain circumstances. This fact, together with the results described above, suggests the hypothesis that the concrete deterioration is caused by the Mg in the ground water a highly probable one. If this is true, then it is very likely that there is other deterioration in the structure that may not be visible from inspection of the inside of the shaft. A coring program that includes the rock-concrete interface may be necessary to determine the extent of this deterioration.

A laboratory simulation involving exposure of concrete to either natural ground water or a laboratory-prepared chemical analog would be most useful for verifying the hypothesis that the ground water is indeed the ultimate cause of the deterioration. If more than one portland cement was used in the construction, then an analysis of its effect on durability in this context would be in order.



Key

Z, sound concrete
Y, partially deteriorated concrete
X, black material
W, chemical grout + crystalline material
V, sanded grout
U, partially deteriorated concrete
T, sound concrete

Figure B1. Lateral view of external features of WIPP-2 DC-4 and DC-5

3 Oct 90
CEWES-SC
Wakeley and Poole

DRAFT INTERIM REPORT
CONDITION OF CONCRETE FROM WIPP WASTE HANDLING SHAFT

INTRODUCTION

1. This draft report is a follow-up to the previous unofficial report to Dr. Jim Nowak of SNL dated 12 September and updated 18 September. Data we have collected through petrography and XRD since 18 September largely are consistent with our previous analyses. Additional data collected by EDX are inconclusive.

2. The previous report described the cores and slabs cut from them, recovered from along the joint at 834 ft. Those descriptions are still valid, and are not repeated.

3. This report offers additional discussion and interpretation of data, some discussion of the interactions among Mg, SO_4, Cl, and portland cement, and discussion of potential ways to fix the problem.

PROBABLE MECHANISMS OF DETERIORATION

4. We are convinced that the cement-paste portion of the concrete at 834 ft is deteriorating actively by interactions with components of the water available and moving along the joint at that depth.

5. Deterioration mechanisms include but are not limited to:

a) Formation of calcium chloroaluminate, apparently in lifts or locations where there was sufficient reactive alumina to form this phase. The presence of chloroaluminate does not necessarily mean that the concrete is deteriorating, only that it is changing from its initial composition. However, this phase is generally softer and somewhat more porous than is calcium silicate hydrate (C-S-H), for example. It may be that where it has formed, the concrete then becomes more susceptible to other mechanisms of change or attack, such as the others listed here.

b) Crystallization of Mg salts and gypsum, causing physical cracking of deteriorated concrete, through both paste and aggregate. At the least, this opens additional pathways for water and ion transfer, and thus accelerates chemical change.

c) Chemical alteration of the paste portion of the concrete by Mg. The following discussion of magnesium attack is compiled from several published references, without attribution. It will be properly presented in our report.

EFFECTS ON CONCRETE OF MAGNESIUM, SULFATE, AND CHLORIDE

6. Magnesium sulfate, of which there appears to be an ample supply in the WIPP brine, is known to wreak more havoc on portland-cement concrete than do most other sulfates. It reacts with aluminates, with $CaOH_2$, and with hydrated calcium silicates. Reactions products include gypsum, brucite, and silica gel, which is free to react with whatever else is available. These reactions proceed freely, because a saturated solution of $Mg(OH)_2$ (brucite) has a pH lower than that required to stabilize C-S-H.

7. There is strong indirect evidence that these reactions are occurring. The porous matrix of the organic grout layer in the 834 joint is infilled with well-crystallized gypsum. Brucite also is present infilling the joint, and is present as a coating on aggregates in the deteriorated concrete.

8. Brucite and the silica gel can react further to form magnesium silicate hydrates (M-S-H). This reaction is known in concrete submerged in seawater, but is not very well understood. Mg-S-H is poorly crystalline, and difficult to identify by XRD (nearly impossible by EDX, there being no unique ions). However, it is reported to be a soft, white material, with virtually no cementing properties, and with an XRD basal spacing at about 8.0. We believe we have identified this phase, particularly in the grout layer, V. This grout has troubled us because it looks like it should be cementitious, but it is very soft material. Data from XRD and EDX do not much resemble those expected from a "normal" cementitious material. This layer is depleted in calcium and silicon, and enriched in magnesium, relative to the normal Portland-cement paste fractions of the concretes above and below it. The probable presence of Mg-S-H here would explain a lot: its unique phase assemblage and chemical composition, its softness, and its misidentification elsewhere as being a clay filler (we originally thought it was, as did Mr. Lankard).

9. Mg-S-H represents the final stage of deterioration by magnesium sulfate reactions. We have identified it nowhere except in this discontinuous grout layer. We suggest that the grout was of a composition originally that was quite different than that of the enclosing concretes. If it contained portland cement, then the chemistry of the material, as it exists now, indicates substantial change has occurred due to the interaction with the ground water.

10. We found virtually no ettringite in any deteriorated concrete or grout. More than trace amounts of ettringite would be interpreted as a cause of deterioration due to sulfate attack. The potential for ettringite-based deterioration exists given the availability of sulfates in the ground water and the presence of aluminates from either the cement or the fly ash used in the mixture. However, ettringite is sometimes unstable in solutions with abundant chloride, such as the ground water available here, in that calcium chloroaluminate forms preferentially.

11. The presence of chloride complicates the issue. NaCl tends to increase aggressive reactions of salts with which it has no common ion, such as magnesium sulfate. Also, both NaCl and $CaCl_2$ increase the solubility of ettringite, causing crystallization of chloroaluminate, as was discussed

previously. Thus, none of the reactions occurring here can be called "sulfate attack" in its usual sense. They are instead magnesium attack, enhanced by the presence and characteristic reactions of chlorides.

COMMENTS ABOUT THE MATERIALS USED IN THE WASTE-SHAFT CONCRETE

12. The cementitious matrix of the concrete is a zero-C_3A cement (Type V). This cement apparently was chosen to make the concrete resistant to classic sulfate attack. However, a Class C fly ash also was used (18% substitution for cement). Relative to Class F fly ashes, C ashes have a higher proportion of crystalline components, which include reactive alumina. (Class F fly ashes are more glassy, with the alumina in a form which is more slowly reactive in a sulfate environment.) So what was gained by using a Type V cement may have been lost to some degree by diluting it with Class C fly ash.

13. Alumina in the C4AF of the cement (16%) is less susceptible to sulfate reactions than is alumina in the fly ash, but in an adequately aggressive environment -- which this is -- even this alumina is reactive. Wherever the content of reactive alumina is high enough, and the concrete was in contact with brine enough, both chloroaluminates and magnesium hydroxide chloride hydrate have formed. This concrete is our first encounter with $Mg_2(OH)\ 3Cl \cdot 4H_2O$, but its signature by XRD is perfect. This is the major white mineral filling voids, cracks, and part of the joint. It represents the extent of interaction among magnesium, chloride, and sulfate phases in this system.

14. It occurred to us in discussions with Bryant Mather that the designers of this waste shaft must not have intended for there to be a bond between the host rock -- presumably mostly halite -- and the concrete. If they had, the concrete would have been salt saturated. Therefore, it should not surprise anyone if there is an-open space between the concrete liner and the wall rock, nor that water is moving down this open space. The experts we consulted (here and at Purdue Univ.) had no chemical fix to suggest to stop reactions taking place between water and concrete along this interface.

15. It seems logical to us that use of a concrete which more nearly approaches a phase assemblage known to be more stable in this environment would decrease the likelihood or at least magnitude of chemical alteration, and thus increase the likelihood of long-term performance. A salt saturated concrete, which makes chloroaluminate by design, might be less susceptible to attack. Stopping the water flow is the most obvious avenue for extending the life of the liner.

16. From the evidence of the concrete at 890 ft, it seems that some of the concrete is in far less jeopardy. This could be because of its original composition, or because it is not in contact with an open water course, or some of each.

17. Repair of the joint at 834 ft would require removal of deteriorated or partially deteriorated concrete and replacing it with a salt-saturated expansive concrete. If deterioration is found to have occurred at the rock-concrete interface, remediation would be very difficult or prohibitive.

30 Nov 90
CEWES//Wakeley

PRELIMINARY COMMENTS ON ANALYSES OF CORES FROM ABOVE AND BELOW THE 834 JOINT, WIPP WASTE HANDLING SHAFT

Summary. The core segments taken from 832 and 836 ft in the waste-handling shaft both show deterioration at the end that was in contact with the host rock. Deterioration is more extensive at 836 ft, below the joint, where the thickness of obviously altered concrete is about 45 mm. Above the joint, at 832, the deteriorated concrete extends about 30 mm into the core from the rock interface.

Evidence of deterioration is the same as that seen along the joint at 834 ft: discoloration and softening of the paste; fractures through paste and around and through aggregates; accumulations of Mg hydroxide and hydroxychloride as rims around aggregate particles and in voids in the paste; and the phase assemblage of the paste, which includes chloroaluminate and Mg compounds, and no phases-expected in "normal" concrete. Away from this reacted zone the concrete is intact and in excellent condition. The apparent mechanism of concrete degradation is reaction with magnesium-bearing brine, available in the annulus between concrete and rock.

The Core Segments. WES received the core segments on 2 Nov 90. These consisted of a single length of concrete core from 832, and a small segment of the "rock" from immediately behind it; and 3 segments of concrete from 836, each about 6 in. long and representing contiguous lengths of the drill hole. The concrete that was in contact with the rock, and presumably exposed to brine, remained intact and attached to the adjacent portion of the core in both cases. When viewed from the drilled surface (circumference), neither core looked particularly reacted when initially inspected.

The "rock" is a semiconsolidated clay material. It was analyzed extensively by XRD. Results of these analyses will follow in a later draft report.

Sampling and Analyses of Concrete. The core segments from the "back" of each drillhole, including concrete from the annular contact, were cut in half along their long axes for observations of fresh surfaces of the concrete. One half was archived. A similar length of unreacted concrete from each depth was prepared for microscopic analysis, including studies of aggregates size and air-void system. These studies were intended to reveal similarities or differences between the concretes in the two lifts represented by these cores.

The paste portion of each deteriorated zone was subjected to extensive microscopic and phase-compositional (XRD) analyses.

The mineral accumulations at aggregate interfaces and in voids were hand-picked and studied by XRD. Accumulations of clays on the broken surfaces of some core segments (origin unknown) also were studied.

Cores were photographed before and after cutting. Copies of appropriate photos will be provided with the follow-on draft report.

Results of Analyses and Preliminary Interpretation. The phase assemblage of the deteriorated concrete at 832 is similar to that above the joint at 834. Likewise, the deteriorated concrete from 836 is similar to that below the 834 joint. The affected paste is discolored, and has lower strength than the adjacent "good" concrete. In both cases, the phase assemblage is consistent with our previous interpretation of chemical reactions between high-magnesium brine and cement paste, essentially replacing all expected phases of hydrated portland cement with either chloroaluminate or (probable but still not confirmed) magnesium silicate hydrates. We need to confirm the presence of Mg-S-H by producing it experimentally and studying the resulting XRD data.

Air-void systems of the two concretes are similar and suggest no additional problem. The maximum aggregate size of the upper lift (832) is 0.75 in. From 836, the maximum aggregate size is 1.75 in. We do not know if this or other differences in aggregates contributed to the apparently enhanced deterioration below the 834 joint. However, we had already observed possible chemical differences in the paste portions of these two concretes (above and below the joint at 834). The waste-handling shaft may be a very unforgiving environment, in which nominally minor changes in concrete composition affect noticeably its ultimate performance.

Recommendation. It is clear to us that there is some deterioration of the concrete shaft liner at its interface with the host rock. Having studied samples from a very limited depth range, we cannot assume that the liner is widely deteriorated. For example, its deterioration may be located in contact with clay seams, or only certain clay seams, or some other geologic peculiarity. Further analyses of the source and movements of the high-Mg brine, and studies of cores through the liner at other depths, both will be required for meaningful recommendations about rehabilitation of the shaft liner system.

APPENDIX C: ANALYSES OF SAMPLES FROM THE 812- AND 890-FT LEVELS

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Background

1. In May 1990, Dr. E. J. Nowak of the Sandia National Laboratories (SNL), asked Dr. Lillian Wakeley and staff of the Structures Laboratory (SL), Waterways Experiment Station (WES), for technical assistance concerning the deteriorated condition of concrete in a shaft of the Waste Isolation Pilot Plant (WIPP). Dr. Nowak arranged to have samples shipped to WES for study and interpretation.

2. Background information about the waste shaft, the concrete liner, and the reasons for the study are in the main text of the report, which also includes descriptions of other samples of the concrete from the WIPP shaft liner studied later in this project.

3. The samples that are the subject of this Appendix were received at WES on 8 June 1990. The shipment included three concrete cores, three granular (grab) samples in individual plastic bags, and a brine sample. The concrete and granular samples had been recovered from the waste shaft liner during May 1990, from depths of 812 and 890 ft. The brine sample came from a collector ring at the bottom of the waste shaft liner. The field identifications and the corresponding SL identifications are given in Table C1. The first three digit number on the field identification indicates the depth in feet, from the top of the shaft at which the sample was drilled or collected. The second three-digit number indicates the orientation in the shaft by degrees. North is zero (000).

Table C1

Descriptions and Identification of Shaft-Liner Samples Received at WES during June 1990

Field ID	SL Serial No.	Description
812-340	WIPP-2 DC-1	Concrete core, diameter 3 in., 5-1/2 in. long
812-265	WIPP-2 DC-2	Concrete core, diameter 3 in., 6-1/2 in. long
890-265	WIPP-2 DC-3	Concrete core, diameter 4 in., 4-1/2 in. long

(Continued)

Table C1 (Concluded)

Field ID	SL Serial No.	Description
812-145	WIPP-2 SM-4	136 g of granular material
812-265	WIPP-2 SM-5	114 g of granular material
890-085	WIPP-2 SM-6	128 g of granular material
0002	WIPP-2 SM-7	1/2 pt of liquid

The only two samples that had the same depth and orientation were the concrete core 812-265 (WIPP-2 DC-2), and the bag of granular material, WIPP-2 SM-5 (the sample numbering system used in the CTD at the time assigned a project-specific prefix [WIPP-2] DC for drilled cores, SM for special material).

Test Procedures

4. The concrete cores, the bags of granular material, and the bottle containing the liquid were labeled and photographed. Cores were photographed along their long axis and perpendicular to their long axis to show their damaged ends. Three duplicate sets of these photographs were sent to Dr. Jim Nowak, SNL, during July 1990. One of the larger pieces of the grab sample from bag WIPP-2 SM-4 also was photographed.

5. The end of core WIPP-2 DC-2 was photographed to show the color changes of material at the damaged end. A photograph of the waste shaft end of this core showing exposed aggregate standing in relief was also made. The concrete cores, as well as a few of the larger pieces of debris from each grab sample, were visually inspected and then examined using a stereomicroscope. Methods of examination are summarized in the Corps of Engineers Handbook for Concrete and Cement, Method CRD-C 57.

6. The approximate pH of sample WIPP-2 SM-7 was obtained. The method used did not correct for the high ionic activity of the fluid.

7. Portions of each sample were examined by X-ray diffraction (XRD). Some XRD samples were of aggregate only, ground to pass a 45 μm (No. 325) sieve. Other XRD samples came from paste concentrates, prepared by dividing and discarding as much of the aggregate from the paste portion as possible. This technique will enhance the XRD results obtained from the paste portion.

A slurry of sample WIPP-2 SM-7 was prepared on a flat XRD sample holder, dried at 100 °C, and examined.

8. Following is a list of sample materials analyzed by XRD and their condition.

- a. A small portion of sample WIPP-2 SM-7 was poured on a flat sample holder and dried at 100 °C. A portion of the sediment below the clear liquid in sample WIPP-2 SM-7 (Figure C5) was rinsed with distilled water several times, dried, and analyzed as an air-dried slurry. The sediment was then treated with dilute hydrochloric (HCl) acid to remove the carbonates, rinsed, and examined as an air-dried slurry.
- b. Small pieces of debris were picked at random from the three grab samples (WIPP-2 SM-4, 5 and 6). The debris from each bag was ground to pass a No. 325 sieve and analyzed by XRD as tightly packed powders.
- c. A slurry of white, apparently crystalline, material that was present on a piece of aggregate in grab sample WIPP-2 SM-5 was prepared in methanol, dried, and analyzed.
- d. Two pieces of aggregate from grab sample WIPP-2 SM-5 that had white material on them were scraped clean, rinsed in distilled water, ground to pass a No. 325 sieve, and prepared as tightly packed powders.
- e. A paste concentrate was prepared from concrete core WIPP-2 DC-1, and examined. The concentrate came from an undamaged portion approximately 5 cm from the end of the core.
- f. Four aggregates were picked at random and removed from core WIPP-2 DC-1, ground to pass a No. 325 sieve, and analyzed.
- g. Core WIPP-2 DC-1 had a 2- to 3-mm-thick crust on its end (Figure C4). A portion of the crust was removed, ground, and analyzed.
- h. A paste concentrate of the brownish, damaged end of WIPP-2 DC-2 was prepared and analyzed.
- i. A paste concentrate was prepared from one of the disconnected pieces from the damaged end of WIPP-2 DC-3.

9. All analyses by X-ray diffraction (XRD) were performed using a Philips 1800 automated powder diffractometer, using nickel-filtered copper radiation.

10. A scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) unit was used to examine pieces of material from the concrete cores and from the grab samples. A sample of the liquid (WIPP-2 SM-7) was also prepared by drying in an oven at 100 °C, and examined with the SEM

and EDX. The samples were prepared for SEM examination by depositing a 200-angstrom* (Å) thick layer of gold on their surfaces. The gold was used to make the samples electrically conductive, to improve imaging. Micrographs of SEM images were made, and EDX data (approximate chemical compositions) were collected as part of these procedures. Samples examined by SEM and EDX are listed below.

a. A sample of oven-dried WIPP-2 SM-7.

b. One piece from each of samples WIPP-2 SM-4, 5, and 6.

c. The white material found on an aggregate from bag WIPP-2 SM-5.

d. Undamaged concrete from core WIPP-2 DC-1 was examined. The specimen came from approximately 5 cm below the exposed (damaged) end.

e. Pieces of the thin crust found at the surface of core WIPP-2 DC-1 were removed. One of these pieces was oriented so that the surface opposite the exposed surface could be examined and analyzed by EDX.

f. The brownish material at the damaged end of core WIPP-2 DC-2 was sampled and prepared for SEM studies.

g. The disconnected portion from the top of core WIPP-2 DC-3 was examined. The slab had several aggregate sockets lined with white crystalline material, which was of particular interest, representing the interface between paste and aggregate.

Results

11. A visual inspection of the concrete cores showed that the coarse aggregates were of carbonate rock types (Figures C1, C2, C3a, and C3b). The paste portion of the concrete was a medium light gray (N6) color (all colors are given in accordance with Goddard 1984).** Cores WIPP-2 DC-2 and 3 showed more damage (Figures C2, C3a, C3b, and C4) than did DC-1 (Figure C1). Figure C5 shows the bottle of fluid from the collector ring. The bottom 2.5 cm is sediment. Figure C6 is one of the grab samples of debris received in plastic bags. The other two samples were similar.

12. The visual inspection of debris from the three grab samples showed they consisted of individual pieces of aggregate, agglomerates of cemented

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* To convert angstroms to nanometers, multiply by 0.1.

** References for Appendices are listed with references at the end of the text, p 30.

material that contained aggregate, and some fine granular material. None of the agglomerates appeared to be concrete. They consisted of brownish and white crystalline material (Figure C9). A stereomicroscope examination of the bagged material showed that the agglomerates were coated with secondary crystalline deposits.

13. Figures C7 and C8 show the exposed end of core WIPP-2 DC-2. Figure C7 shows the gradation of apparent deterioration into the concrete. The first centimetre of material in from the exposed end is a moderate yellowish brown (10 YR 5/4) color. This area is soft and easily scaled off. The concrete adjacent to the soft material has a brownish black (5 YR 2/1) color. This area, about 1 cm thick, appears only to be wet from brine and hygroscopic. Damage is not obvious. The rest of the core is undamaged concrete, medium light gray (N-6) in color. Figure C8 is the exposed end surface of core WIPP-2 DC-2. The aggregate stands above the surrounding paste.

14. The pH obtained from sample WIPP-2 SM-7 liquid was 4.3. This value is uncorrected for ionic activity and indicates only that the pH is acid (below neutral).

15. The attempt at XRD of the dried material from WIPP-2 SM-7 was unsuccessful. The dried material was so hygroscopic that the sample would reslurry while being examined and before a useful XRD scan could be obtained. Figure A10 is an EDX spectrum taken from a subsample of the dried material. Chlorine (Cl), calcium (Ca), and oxygen (O) are the main elements present. Potassium (K), aluminum (Al), magnesium (Mg), sodium (Na), and carbon (C) are present. The sample came from clear liquid above the sediments in the bottle. The liquid was quite viscous (high surface tension). The XRD examination of the sediments that settled out of the liquid revealed mainly dolomite, with some calcite, quartz, feldspar, and a trace of clay. No portland cement phases, either hydrated or unhydrated, were present.

16. The crystalline phases that were identified by XRD in the hand picked debris from the three grab samples are listed in Table C2 and discussed in the following paragraphs.

Table C2

Crystalline Phases Identified by XRD in Grab Samples

WIPP-2 SM-4	WIPP-2 SM-5	WIPP-2 SM-6
812-145	812-265	890-085
Gypsum ($CaSO_4 \cdot 2H$)	Chloroaluminate	Gypsum
Calcium Sulfate Hemihydrate	Halite	Calcium Sulfate Hemihydrate
($CaSO_4 \cdot 1/2H$)	Brucite	Brucite
Brucite ($Mg(OH)_2$)	$Mg_2(OH)_3Cl \cdot 4H_2O$	Halite
Sylvite (KCl)		
812-145	812-265	890-085
Halite (NaCl)		
Chloroaluminate		

17. WIPP-2 SM-4: Figure C11 is an EDX spectrum showing the chemical composition of chloroaluminate crystals seen in Figure C12. Iron is present in the crystal structure. The micrograph and spectrum were made of crystals found in an aggregate socket. The socket is shown in Figure C9.

18. WIPP-2 SM-5: The piece of debris examined from this sample did not show any sulfate minerals by XRD. Figure C14 shows the dolomite aggregate with other crystalline material on it. Figure C13 is the EDX spectrum made from the total area in Figure C15. The spectrum shows Mg, Cl, and O as the main elements. A trace of Ca is present. The XRD scan of the white material showed two crystalline phases: brucite and an unnamed phase with the chemical composition magnesium hydroxide chloride hydrate ($Mg_2(OH)_3Cl \cdot 4H_2O$). This aggregate, and another examined by XRD from the same grab sample, was dolomite.

19. WIPP-2 SM-6: This sample contained gypsum and calcium sulfate hemihydrate, as did WIPP-2 SM-4. Figure C16 is an EDX spectrum of one of these phases. It is impossible to differentiate these phases by EDX because the method detects Ca, S, and O. The hydrogen present in the water is not detected.

20. There was some evidence suggesting acid etching of concrete and aggregates. Figures C17 and C18 are SEM images of aggregates showing possible etching. These aggregates are from sample WIPP-2 SM-6.

21. The composition of the undamaged hydrated paste concentrate examined from sample WIPP-2 DC-1 was as expected from a portland-cement concrete. The hydrated phases were mainly calcium-silicate-hydrate (C-S-H), and calcium hydroxide (CH). Traces of hemicarboaluminate and ettringite were present. No unhydrated portland cement phases were identified. Figure C19 is an EDX spectrum of the paste. The minimal presence of chlorine suggests that the chlorine ion may have migrated from the wall of the shaft liner into the concrete to a depth of at least 5 cm, where this sample was taken. Figure C20 is an SEM micrograph of the paste. Calcium hydroxide (CH) and C-S-H gel are visible in the micrograph.

22. The four aggregates randomly picked from core WIPP-2 DC-1 and examined by XRD consisted of dolomite and calcite. The major phase in each was dolomite. They also showed a trace of quartz.

23. The thin crust present on the end of core WIPP-2 DC-1 (Figure 4), consisted of gypsum, brucite, aragonite, calcite, and dolomite. Some of the calcite, and all of the dolomite, probably came from the aggregate. No halite or sylvite was detected by XRD. Figure C21 is an EDX spectrum of gypsum and brucite found in the crust by SEM. The spectrum was collected on an area with no apparent distinctive crystal forms. Mg, O, S, Ca, and Cl are the elements present.

24. The end portion of core WIPP-2 DC-2 was quite soft. This moderate yellowish brown (10 YR 5/4) material represented severely damaged paste. Damage is more apparent in this core than it was in the other two cores. Figure 7 shows the three distinct bands of the damaged end of the core. The most obviously damaged zone, the first centimetre in from the exposed end of the core, is a moderate yellowish brown (10 YR 5/4) color. The next 1 cm, which appears continually wet but shows no other apparent damage, is brownish black (5 YR 2/1). The rest of this core is a medium light gray (N6) color and appears to be normal concrete. The XRD examination of the soft material at the end of the core showed it consisted of chloroaluminate, gypsum, halite (NaCl), and sylvite (KCl). This material had a stronger basal XRD peak of chloroaluminate (at 7.81Å) than any of the other materials examined. Figure C22 is an EDX spectrum of chloroaluminate crystals shown in Figure C23. The spectrum, as well as all other spectra of chloroaluminate in these samples, shows iron (Fe) substituted into the chloroaluminate structure.

25. Core WIPP-2 DC-3 (890-265) had two thin slabs separated from the end of the core during drilling and recovery (Figure C3b). At least one coarse aggregate particle was split between these slabs, giving an appearance similar to damage from freezing and thawing. Sockets (the "negative" of the aggregate) left in the paste portion were coated with a white crystalline layer, shown in Figure C24. This SEM image came from crystals still attached to an aggregate that had pulled away and left a socket. Figure C25 is an EDX spectrum from the square area in Figure C24. The spectrum suggests that although brucite was not identified by XRD, other poorly crystalline Mg-Ca phases are possible. The XRD examination of the paste concentrate taken from one of the slabs identified chloroaluminate and CH.

Discussion

26. The visual and stereoscopic examination of the concrete cores showed that the bulk of the concrete sampled was in good condition. Note that these core segments represent only the first 15 to 18 cm from the inner surface of a shaft liner that is between 50 and 120 cm thick. The hydrated phases present in the undamaged paste were normal hydration phases for portland cement. No unhydrated portland cement was identified by XRD. The mineralogy of the coarse aggregate that was examined by XRD was mainly dolomite. Some calcite was present in some of the aggregates. The Mg content of the coarse aggregate was high.

27. Although we were unable to determine accurately the pH of the brine sample, our observations and data provided by SNL indicate that the pH is below neutral (at least weakly acidic). The solution is high in Cl, Ca, and O. Potassium, Mg, and Al are also present. Since the SEM examination indicated acid etching on the surfaces of some aggregates and the aggregates in one of the samples stand out in relief above the surrounding paste, it is possible that the concrete on the exposed inner perimeter of the shaft liner has been affected by mild acid attack. The mechanism postulated is formation of carbonic acid due to the strong positive airflow in the shaft and interactions with brine. If this is occurring, it is a minor mechanism of deterioration of the exposed concrete.

28. Several phases that could be detrimental to concrete were identified in the grab samples and from the damaged ends of the cores. Halite was identified in the damaged portions of the cores, as well as the debris from

the grab samples. Gypsum and calcium sulfate hemihydrate were present in two of the grab samples, and gypsum was present in two concrete cores. Brucite was present in all the grab samples. A phase with chemical composition $Mg_2(OH)_3Cl \cdot 4H_2O$ (powder diffraction file No. 7-412) was also present in one grab sample. Brucite can be harmful to concrete if it forms more than just coatings on aggregates (Massazza 1985). The $Mg_2(OH)_3Cl \cdot 4H_2O$ almost certainly imparts no strength to cement paste. Brucite was found to be present at the aggregate-paste interface. It may be an alteration product from the dolomite or a product of complex interactions between $Ca(OH)_2$, $CaSO_4$, and magnesium salts, as described by Massazza (1985). Calcium chloroaluminates and probably calcium chloroferrites are abundant in two of the grab samples. These phases were also present in the damaged ends of the cores. The high iron (Fe) content found by EDX in crystals of chloroaluminate shows that Fe is a major cation in the structure. All of these phases could cause deterioration of already-set concrete.

29. The debris in the grab samples show no evidence of hydrated cement phases. We presume this indicates their total demise, rather than that they never were present. Aggregates are loosely agglomerated by precipitated salts and brucite, but there are no strength-giving components.

Conclusions

30. Deterioration of the waste-shaft concrete is tentatively attributed to chemical interaction between the brine available in overlying brine aquifers and the cement paste. This brine gains access to the inner perimeter of the liner and flows down the shaft and across the face of the concrete. These solutions, containing Cl and Fe, form calcium chloroaluminate and calcium chloroferrite. This begins the process of deterioration of the concrete, because these phases impart very low strength. Other mechanisms that may contribute to deterioration are the formation of brucite at the aggregate/paste interface, possibly related to alteration of the dolomite in the aggregate; the formation of halite during periods of drying, causing fractures to remain open to further fluid ingress; and some minor damage caused by acid attack.

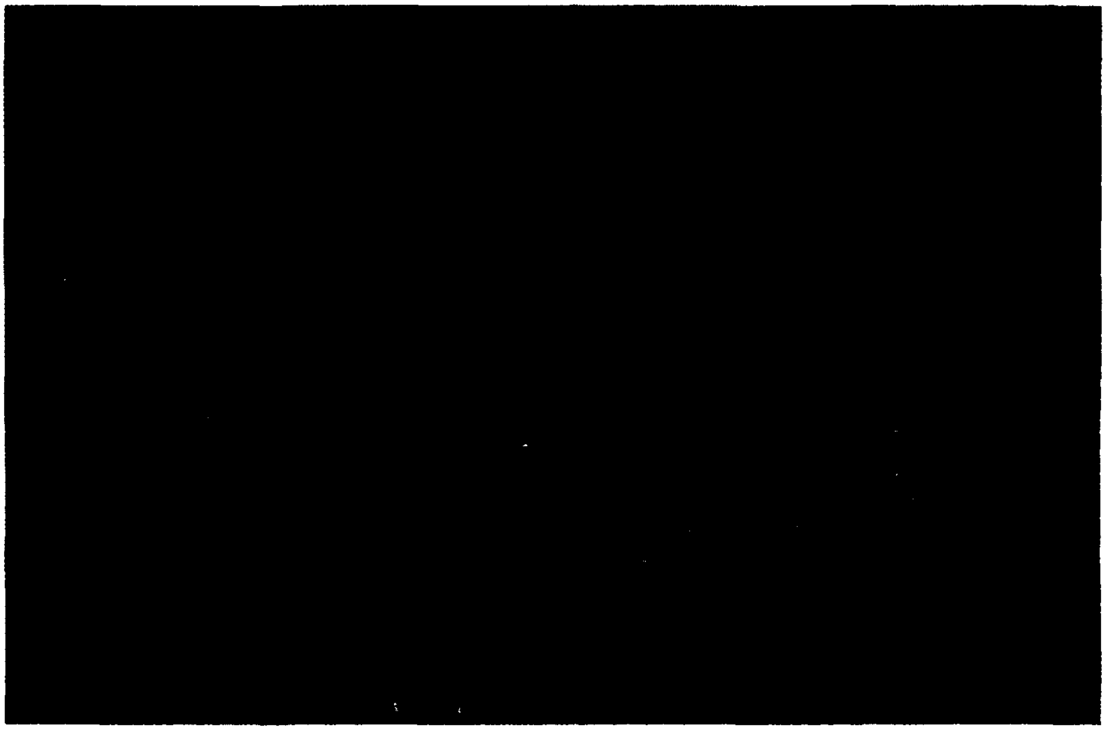

Figure C1. Core 812-340 (WIPP-2 DC-1). Discolored zone at left was surface of concrete liner exposed in waste shaft

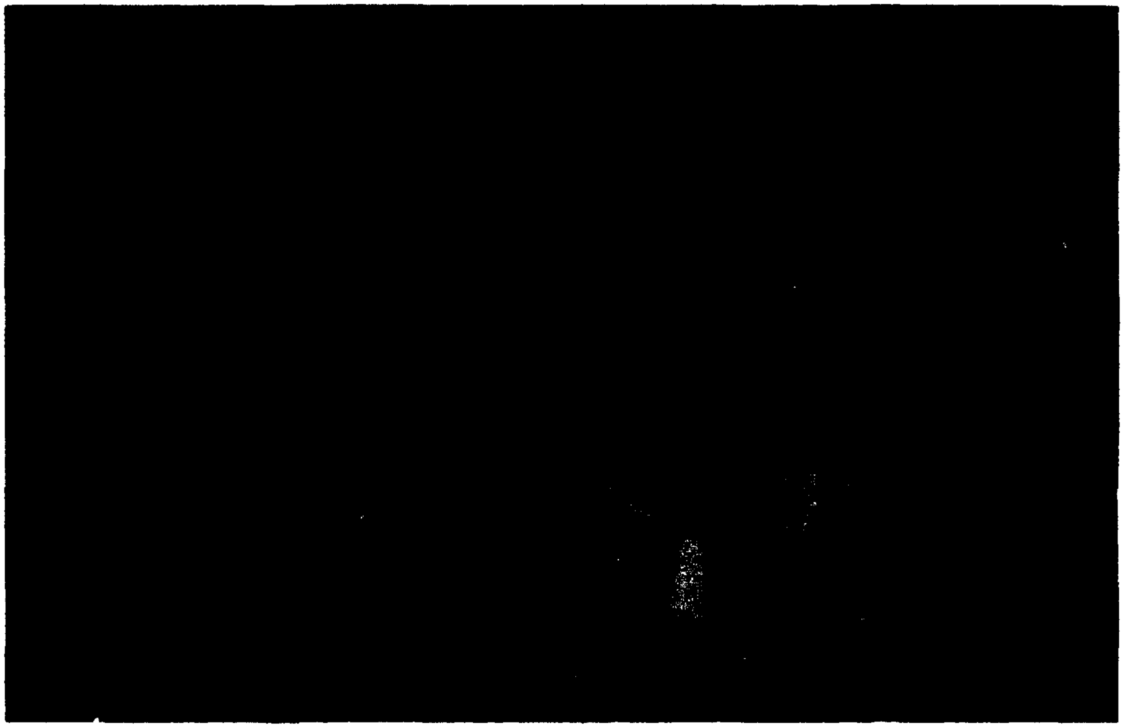

Figure C2. Core 812-265 (WIPP-2 DC-2). Discolored zone at left (about 4 cm thick) was surface of liner exposed in waste shaft

Figure C3a. Core 890-265 (WIPP-2 DC-3), view along axis of core; left is exposed end. Damaged concrete broke away from exposed end during drilling and recovery of core

Figure C3b. Core 890-265, exposed end view, showing damaged zone broken away during drilling and recovery of core

Figure C4. Cores 890-265 (WIPP-2 DC-3), 812-340 (WIPP-2 DC-1), 812-265 (WIPP-2 DC-2), exposed end views showing damaged surface of liner in waste shaft

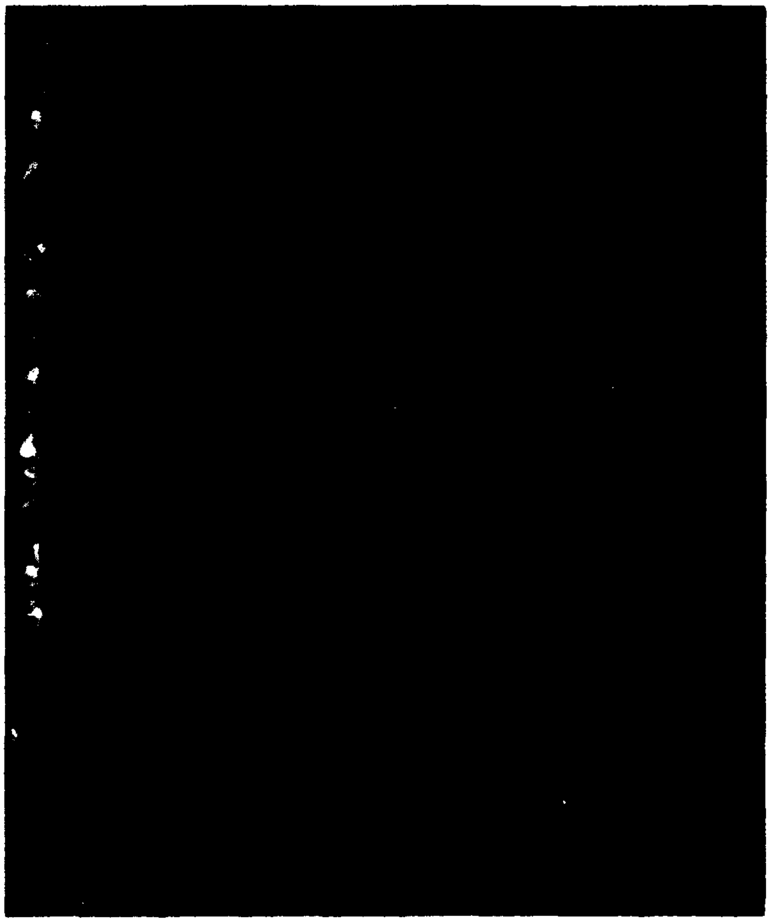

Figure C5. Sample 0002 (WIPP-2 SM-7). Bottled brine with solids collected from bottom water ring

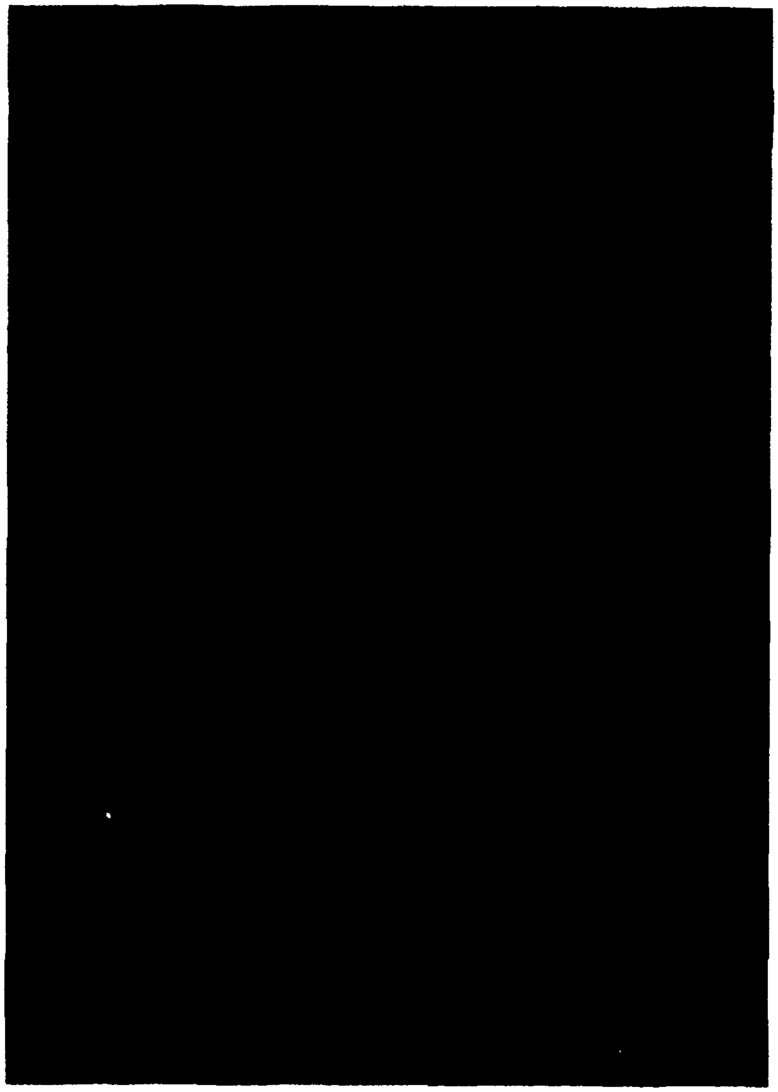

Figure C6. Grab sample 890-085 (WIPP-2 SM-3). Shows damaged debris; this is typical of the other grab samples

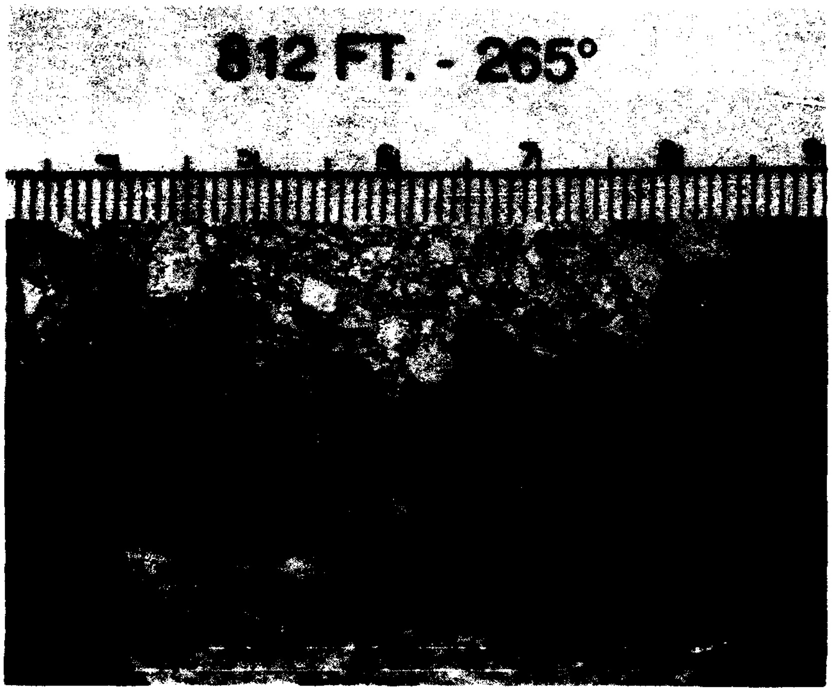

Figure C7. Core 812-265 (WIPP-2 DC-2). View of three distinct conditions of the concrete liner exposed in waste shaft

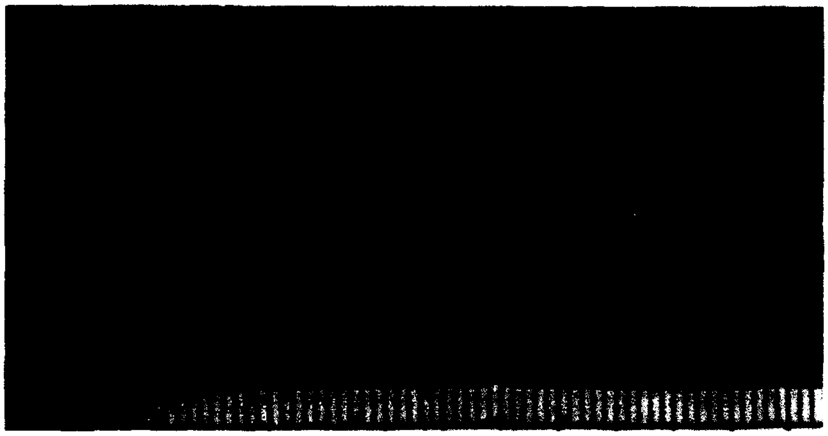

Figure C8. Core 812-265 (WIPP-2 DC-2) X1.5. View of exposed surface of liner showing aggregate in relief. Each mark on ruler is 1 mm

Figure C9. Grab sample 812-145 (WIPP-2 SM-4). View of debris showing white deposits over the surface. The square shows where the EDX spectrum, Figure 11, and the Photomicrograph, Figure 12, came from

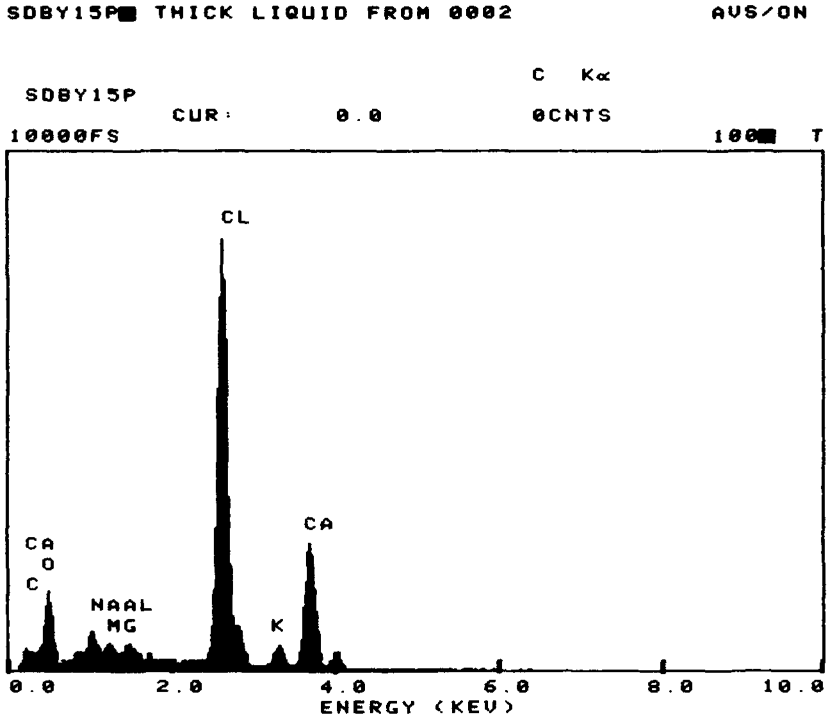

Figure C10. Liquid 0002 (WIPP-2 SM-7). EDX spectrum showing approximate chemical composition of the brine

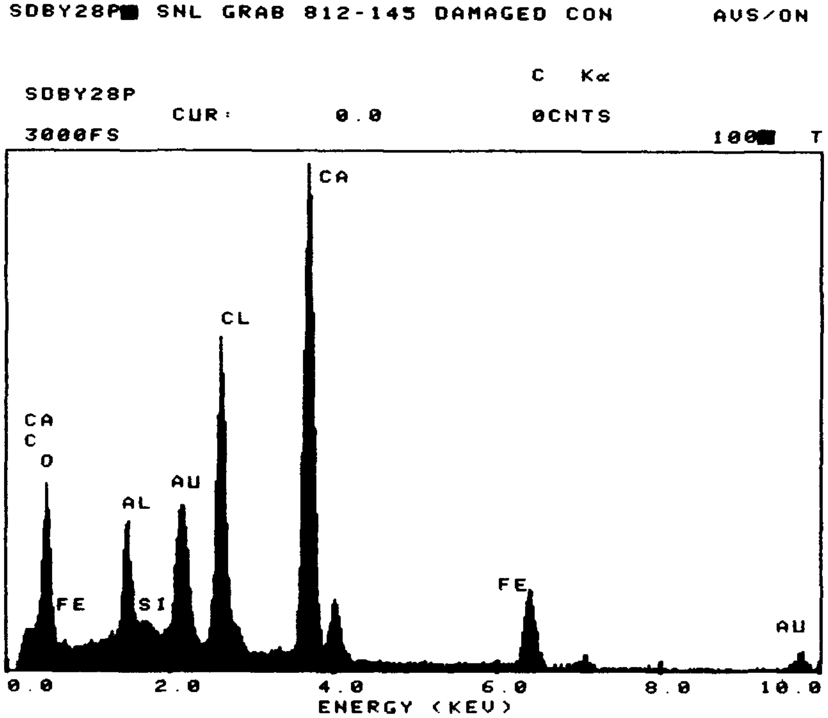

Figure C11. Grab sample 812-145 (WIPP-2 SM-4). EDX spectrum of crystals shown in Figure 12. Note the iron in structure

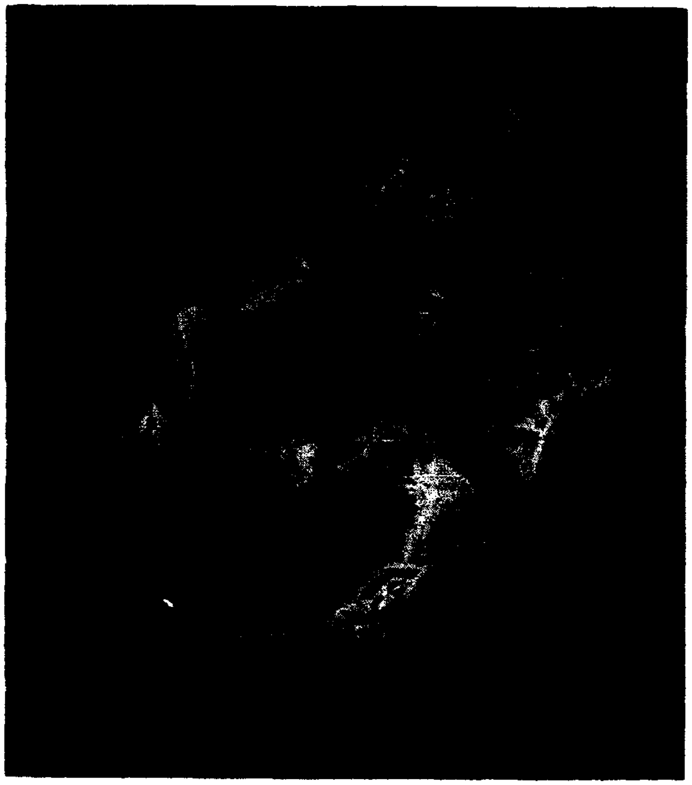

Figure C12. Grab sample 812-145 (WIPP-2 SM-4). Crystals of chloroaluminate. Figure 11 shows the chemistry of these crystals

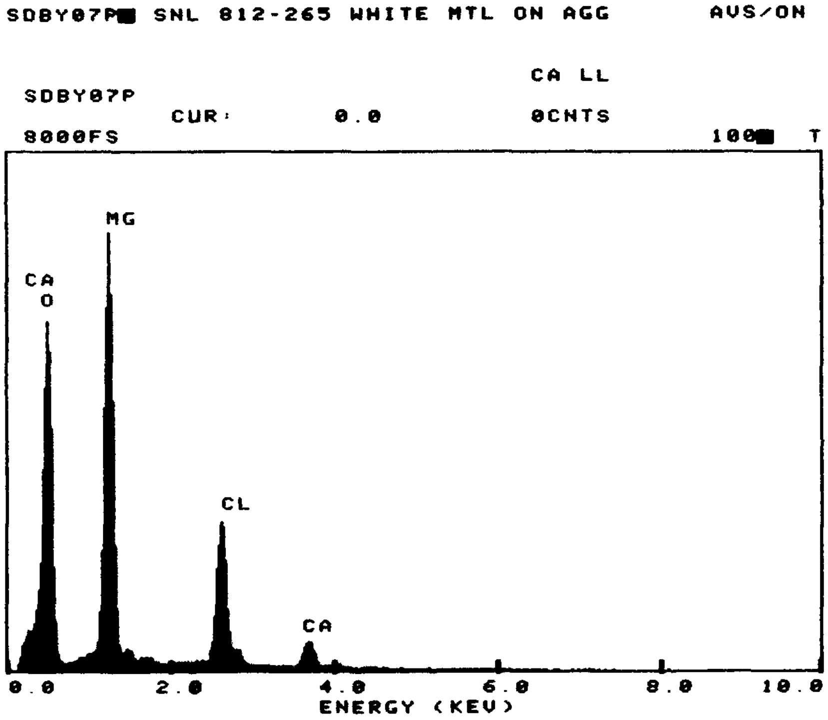

Figure C13. Grab sample 812-265 (WIPP-2 SM-5). EDX spectrum of crystals shown in Figure 15

Figure C14. Grab sample 812-265 (WIPP-2 SM-5). White deposit on a coarse aggregate

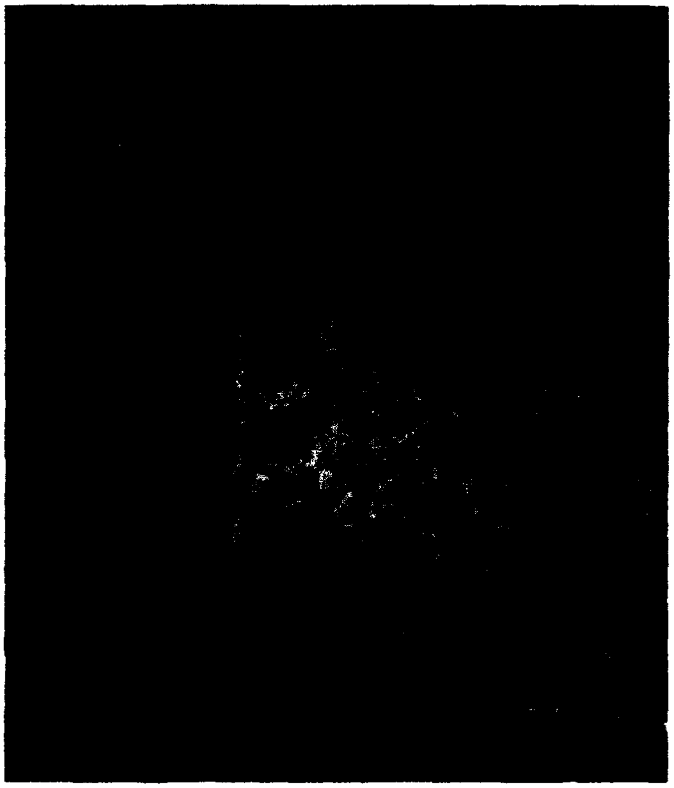

Figure C15. Grab sample 812-265 (WIPP-2 SM-5). Brucite and $Mg_2(OH)_3Cl \cdot 4H_2O$ crystals in the square in Figure 14

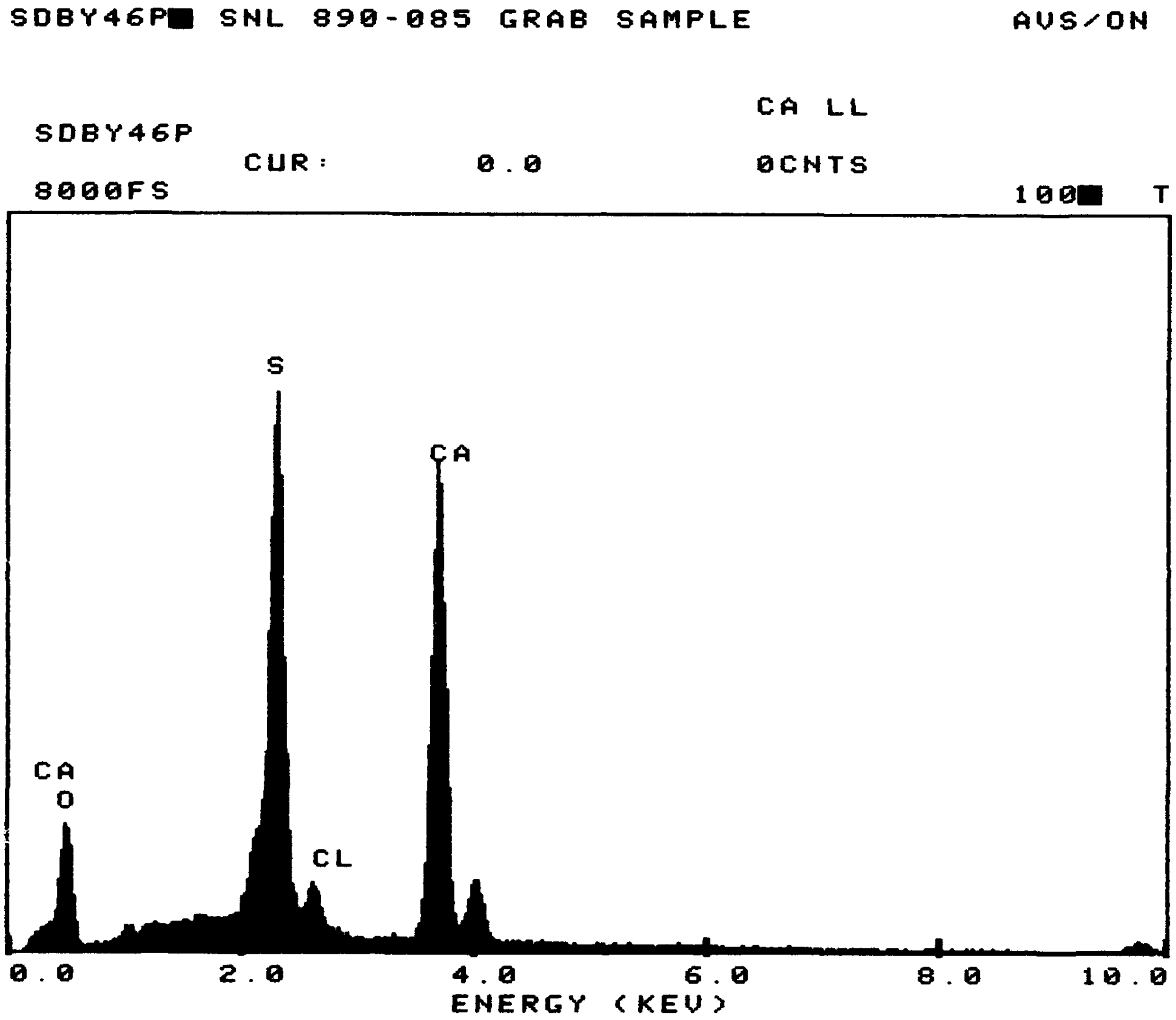

Figure C16. Grab sample 890-085 (WIPP-2 SM-6). EDX spectrum of gypsum or calcium sulfate hemihydrate

Figure C17. Grab sample 890-085 (WIPP-2 SM-6). Aggregate surface that was exposed to brine

Figure C18. Grab sample 890-085 (WIPP-2 SM-6). Aggregate surface that was exposed to brine. Coccoliths in left center appear etched

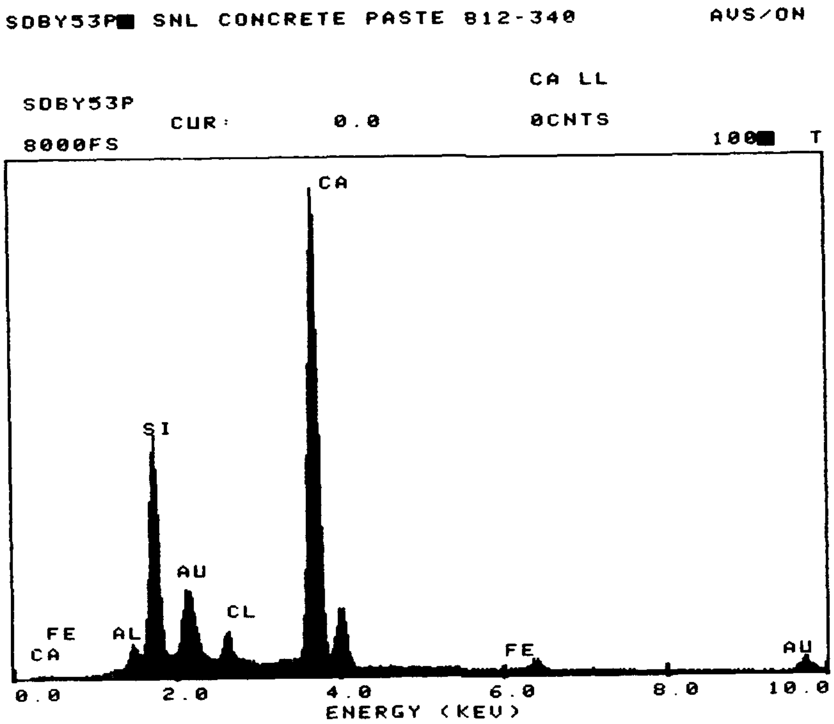

Figure C19. Core 812-340 (WIPP-2 DC-1). EDX spectrum of undamaged paste

Figure C20. Core 812-340 (WIPP-2 DC-1). Undamaged paste about 2 in. from the waste shaft surface

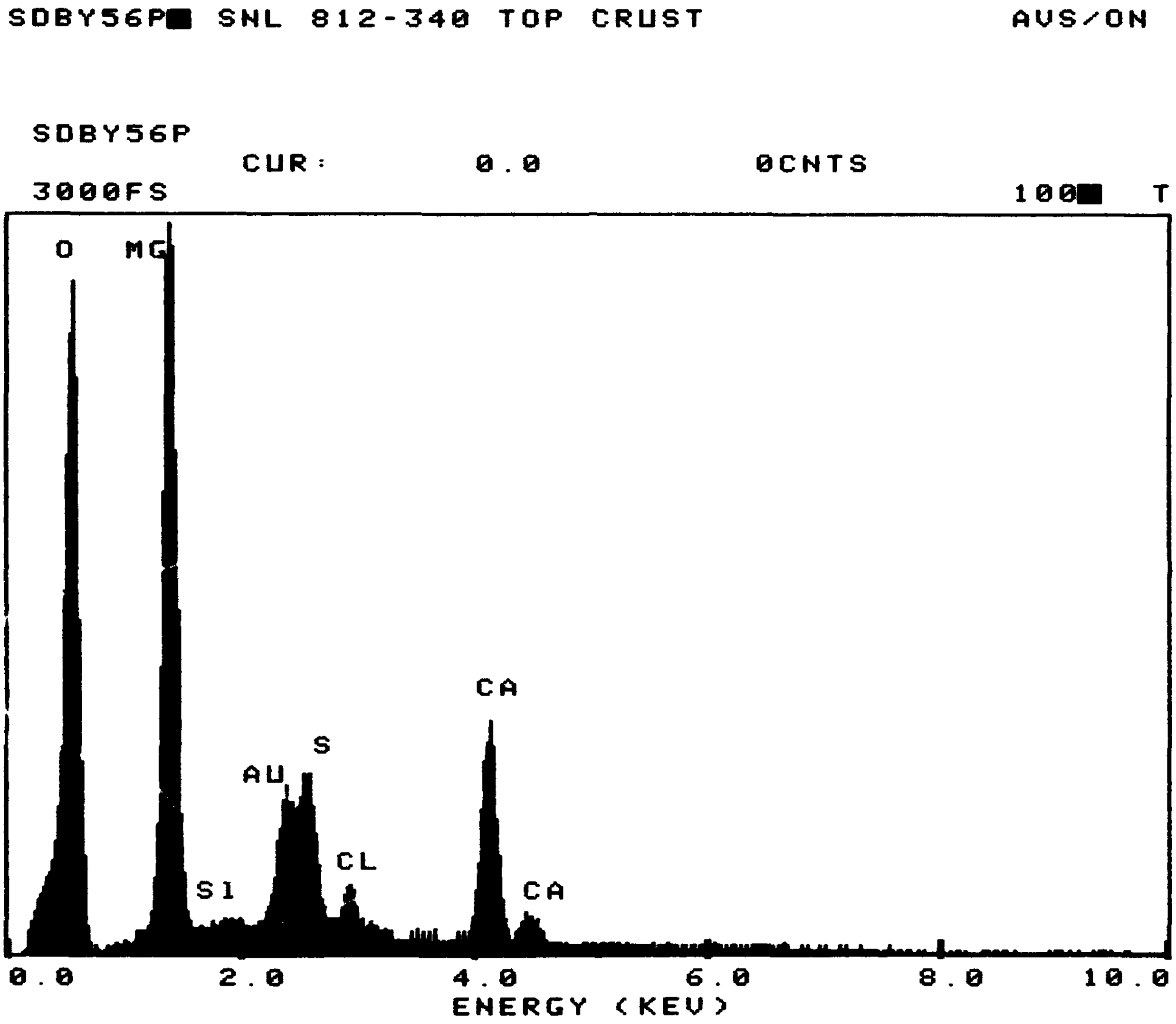

Figure C21. Core 812-340 (WIPP-2 DC-1). EDX spectrum of brucite and gypsum

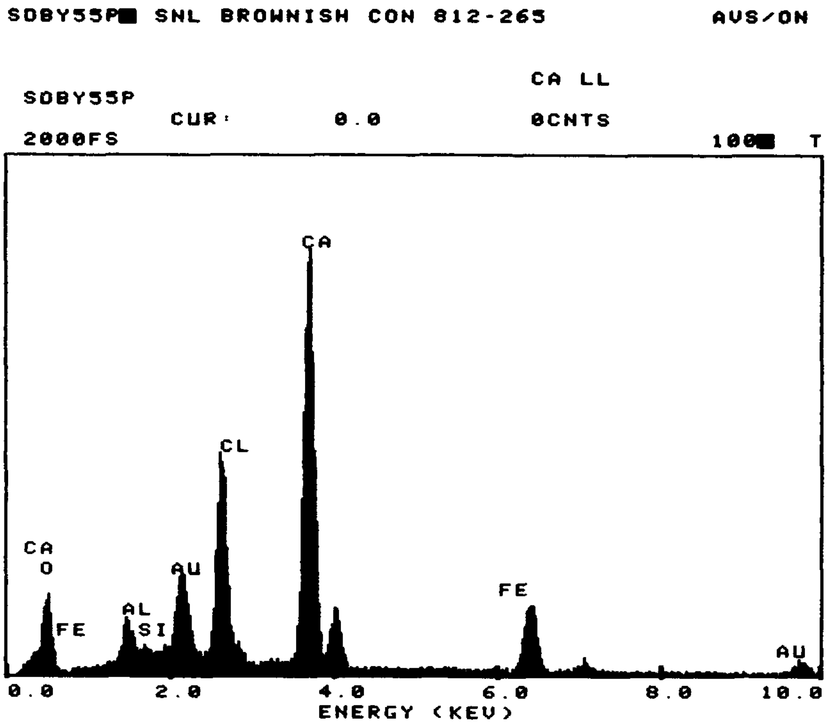

Figure C22. Core 812-265 (WIPP-2 DC-2). EDX spectrum of chloroaluminate crystals shown in Figure 23

Figure C23. Core 812-265 (WIPP-2 DC-2). Crystals of chloroaluminate. The spectrum in Figure 22 came from the square

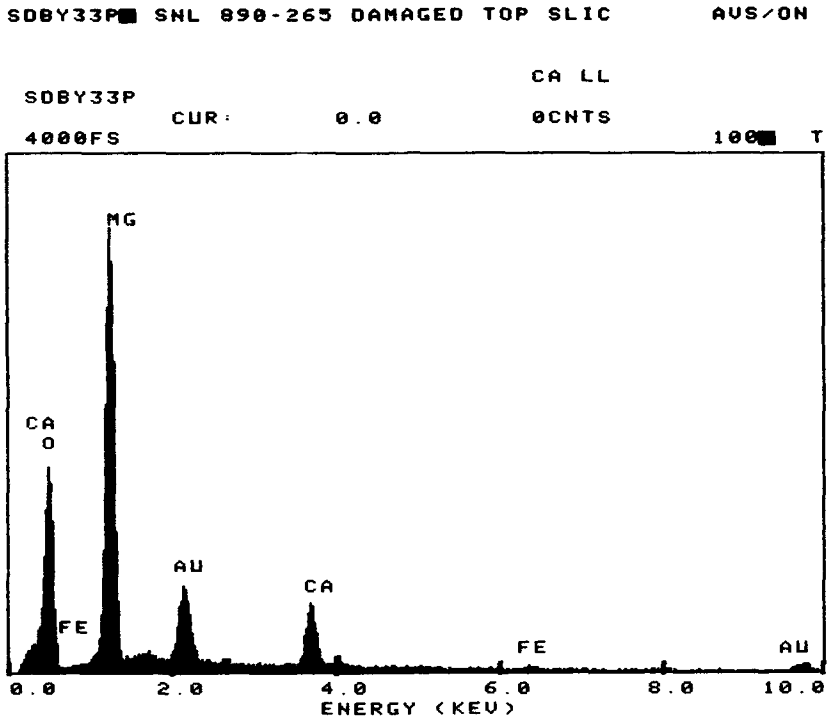

Figure C24. Core 890-265 (WIPP-2 DC-3). EDX spectrum of brucite; also, calcium is present

Figure C25. Core 890-265 (WIPP-2 DC-3). This shows deposits of brucite. Figure 24 came from the square. Chloroaluminate crystals are shown in upper right corner

APPENDIX D: REFERENCE DATA FOR CRYSTALLINE PHASES IDENTIFIED BY X-RAY DIFFRACTION

MINERAL OR CHEMICAL NAME	CHEMICAL FORMULA	JCPDS* Ref. #
Portlandite	$Ca(OH)_2$	4-733
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26\ H_2O$	37-1476
Calcium Chloroaluminate	$Ca_4Al_2O_6Cl_2 \cdot 10\ H_2O$	35-105
Brucite	$Mg(OH)_2$	7-239
Magnesium Silicate Hydrate	N.A.	N.A.
Calcium Silicate Hydrate	$(Ca, K, Na, H_3O)(Si, Al)O_8 \cdot H_2O$	20-544
Halite	$NaCl$	5-628
Quartz	SiO_2	33-1161
Dolomite	$CaMg(CO_3)_2$	36-426
Magnesium Chloride Hydroxide Hydrate	$Mg_2(OH)_3Cl \cdot 4\ H_2O$	7-412
Gypsum	$CaSO_4 \cdot 2\ H_2O$	33-311
Sylvite	KCl	4-587
Bischofite	$MgCl_2 \cdot 6\ H_2O$	25-515
Calcium Aluminum Oxide Carbonate Hydrate	$Ca_8Al_4O_{14}CO_2 \cdot 24\ H_2O$	36-129
Calcite	$CaCO_3$	5-586

N.A. = Not Available

* Joint Committee on Powder Diffraction Standards International Centre for Diffraction Data 1988

APPENDIX E: EDX DATA

A cross section of core WIPP-2 DC-5 was analyzed by energy-dispersive X-ray fluorescence (EDX) using a Princeton Gamma Tech (PGT) attachment to a Hitachi S 2500 scanning electron microscope (SEM) for evidence of changes in chemical composition among the layers T - Z, described in Figures 2 and 3 of the main body of the report.

Sodium (Na) and chlorine (Cl) distributions across the specimen were determined by analyses at 4-mm intervals along a transect from the center of the Z layer through the center of the T layer. No particular effort was made to separate paste and aggregate fractions in this analysis. A magnification of 150x was used, with a single spectrum collected at each point. Results were interpreted by the "no standards" program, consequently, results best indicate relative relationships rather than absolute percentages. Results of this analysis are presented in Figure E1.

Distributions of calcium (Ca), silicon (Si), aluminum (Al), iron (Fe), magnesium (Mg), sodium (Na), potassium (K), and chlorine (Cl) were determined separately for paste and aggregate fractions in each layer by choosing areas for analysis that appeared in the SEM window to be purely of that fraction. This required variation in magnification. Five independent spots were analyzed for each fraction in each layer. Each of these analyses were represented by a single spectrum taken at each spot. Results were interpreted by the "no standards" program. Percentages represent mass percentage of each element; i.e., no oxide conversion was done. Results of these analyses are summarized in Tables E1 and E2.

Table E1

Elemental Analysis (± s.e.[1]) of Paste Fraction of Each Layer of Specimen WIPP-2 DC-5

Element	Layers				
	Z	Y	V	U	T
Si	9.7 ± 1.0	9.8 ± 0.9	2.8 ± 1.1	12.6 ± 0.3	12.6 ± 1.9
Al	2.3 ± 0.2	2.2 ± 0.1	0.5 ± 0.3	2.8 ± 0.2	3.5 ± 0.8
Fe	2.3 ± 0.2	2.5 ± 0.2	1.1 ± 0.2	2.8 ± 0.1	2.9 ± 0.4
Ca	43.7 ± 2.3	36.1 ± 1.8	5.1 ± 1.4	32.4 ± 0.3	34.0 ± 3.8
Mg	2.0 ± 0.1	1.8 ± 0.2	11.8 ± 2.3	1.8 ± 0.2	3.1 ± 0.8
S	0.6 ± 0.1	1.0 ± 0.1	0.7 ± 0.2	1.3 ± 0.0	0.7 ± 0.1
Na	n.d.[2]	n.d.	9.6 ± 2.6	n.d.	n.d.
K	0.5 ± 0.0	0.8 ± 0.3	6.2 ± 0.7	0.4 ± 0.1	0.6 ± 0.1
Cl	4.3 ± 0.5	12.2 ± 0.4	35.0 ± 4.1	10.2 ± 0.4	6.1 ± 0.3
Sum PC[3]	58.1 ± 1.0	50.6 ± 0.7	9.5 ± 2.6	50.3 ± 0.2	53.0 ± 0.8

[1] s.e. = standard error of the mean of analyses over 5 spots
[2] n.d. = none detected
[3] Sum PC = sum of the elements that constitute the major fraction of portland cement: Ca, Si, Al, Fe

Table E2

Elemental Analysis (± s.e.[1]) of Coarse-Aggregate Fraction of Each Layer of Specimen WIPP-5 DC-2. Na, K, and S were at Undectable Levels

Element	Layer				
	Z	Y	V	U	T
Si	1.7 ± 0.2	1.3 ± 0.3	No Coarse Aggregate	2.0 ± 0.3	3.3 ± 0.7
Al	2.1 ± 0.1	2.0 ± 0.0		2.6 ± 0.2	3.0 ± 0.2
Fe	0.5 ± 0.1	0.2 ± 0.0		0.3 ± 0.1	0.4 ± 0.0
Ca	21.4 ± 0.9	21.8 ± 0.4		22.2 ± 0.8	21.1 ± 0.8
Mg	37.0 ± 0.9	36.9 ± 0.4		35.4 ± 0.8	35.0 ± 0.6
Cl	0.4 ± 0.1	1.2 ± 0.2		0.7 ± 0.1	0.6 ± 0.1

[1] s.e. = standard error of the mean of analyses over 5 spots

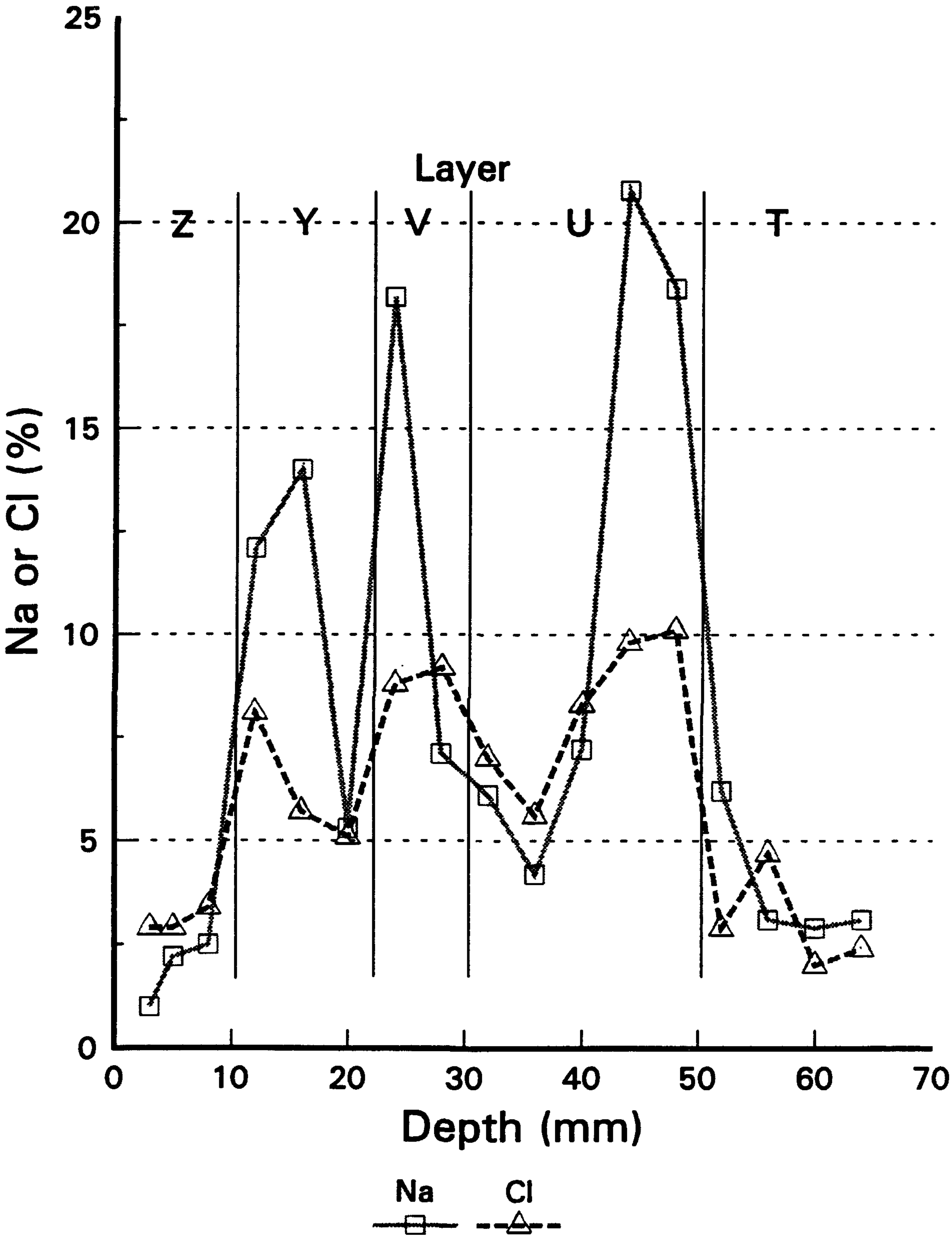

Figure E1. Distribution of Na and Cl across WIPP-4 DC-5

Waterways Experiment Station Cataloging-in-Publication Data

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