Stanley Consultants INC.

MEETING NOTES
Final 5/5/2015

Meeting Dates: October 7 – 8, 2014

Meeting Notes Submittal Dates: January 15, 2014 – Submitted to NDEP

Place: October 7 – NV Energy Reid Gardner Station
Moapa, Nevada
October 8 –NV Energy Pearson Building
Las Vegas, Nevada

Project/Purpose: NV Energy - Reid Gardner Station
Implementation of Administrative Order on Consent (AOC)
Muddy River Investigation Technical Meeting and Site Visit

Attendees:

10/7	10/8	
X	X	Alison Oakley/NDEP
X	X	Scott Smale/NDEP
X	X	Brad Cross/ARCADIS U.S., Inc.
X	X	John Kivett/ARCADIS U.S. Inc.
X	X	Michael Shivell/ACADIS U.S. Inc.
X	X	Julie Sueker/ACADIS U.S. Inc.
X	X	David Hull/ARCADIS U.S., Inc.
X	X	Tony Garcia/ NV Energy
X	X	Mike Rojo/NV Energy
X	X	Jason Reed/NV Energy
X	--	Ann Casey/NV Energy (via telephone)
X	X	Scott Dethloff/CH2M Hill
X	--	Mark Andersen/CDWR
X	X	Sergio Escobar/CDWR
X	X	Peter Mesard/Exponent
X	X	Joseph Scalia/ Exponent
X	X	Becky Svatos/Stanley Consultants
X	X	Todd Knause/Stanley Consultants
X	X	Africa Espina/Stanley Consultants
X	X	Jonathan Sarich/Stanley Consultants
X	X	Brad Bessinger/ S.S. Papadopulos & Associates, Inc.

Notes By: Julie Oriano/Stanley Consultants

A meeting was held between NV Energy and Nevada Division of Environmental Protection (NDEP)

representatives on October 7 and 8, 2014. This was a technical meeting and site visit to develop and outline data collection objectives for the Muddy River Investigation Work Plan, present preliminary findings of the geochemical conceptual site model (CSM), and discuss applicable regulations related to the Muddy River. Topics discussed during the meeting are summarized below.

October 7

Reid Gardner Station (Station) Site Tour –Meeting attendees toured the Station, ponds, mesa, raw water ponds, diversion dam, South Gate Spring, and Muddy River. The effects of recent Muddy River flooding were observed.

- Action Item: NV Energy to conduct observations of the Muddy River while the vegetation on the banks is still sparse. This includes looking for seeps and changes to the river caused by the flooding.

Meeting Goals **–**The Muddy River Work Plan to be submitted to NDEP by the end of 2014 will focus on the Muddy River as a receptor, and the data gathered will be focused on the Muddy River and immediately adjacent groundwater. NV Energy plans to begin implementation of this Work Plan in February 2015. The scope of the investigations to be included in this Work Plan will be developed with NDEP during this meeting. Three additional Work Plans will be submitted to NDEP in the first quarter of 2015 for investigations in the areas of the 4B and 4C Ponds (PA-2), 4A Pond (PA-3), and the D, E, F, and G Ponds (PA-5-7) that will address data collection in those areas. NV Energy plans to begin implementation of these three Work Plans by April 2015. The next quarterly AOC meeting with NDEP in December 2014 will focus on developing the objectives and scope of the investigations to be included in these three Work Plans.

Background **–** Stanley Consultants/NV Energy presented a history of the Station and its operations, pond history, pond source area characterization to date, geology, hydrogeology, and potential future Station uses. The seven draft geologic cross-sections provided to NDEP prior to the meeting were discussed and ARCADIS requested changes to the cross-sections in the future. NDEP may also request additional transects in the future, for example, one that is oriented in an east-west direction along the south side of the E Ponds.

The pathways and receptors related to the ponds and the Muddy River were discussed. Potential receptors related to the ponds include the Muddy River, Station workers, the offsite downgradient drinking water well at the Hidden Valley Ranch (former Dairy), and downgradient irrigation wells.

A preliminary list of 12 constituents of concern (COCs) related to the Muddy River was discussed with NDEP. Nevada regulations that apply to the Muddy River and the regulatory requirements to obtain an exemption from further groundwater corrective action were discussed.

- Action Item: NV Energy to prepare a memo for NDEP review that discusses the current Muddy River water quality. Available Muddy River water quality data will be compared to applicable water quality standards; upstream to downstream water quality changes will also be evaluated.

The memo will identify a list of water quality parameters NV Energy believes should be used to evaluate potential groundwater impacts to the Muddy River in the area of the Station.

August Field Events – NV Energy provided NDEP with available results of the August 2014 Muddy River field investigations prior to the meeting. This information was discussed during the meeting along with lessons learned from the field investigations. The preliminary Muddy River field investigations were completed; however, the groundwater monitoring event had to be stopped on September 8 due to Muddy River flooding. At the time of the meeting, the laboratory data from the August investigations were not yet available. The remaining 13 wells will be sampled in October and a complete set of groundwater elevations will also be obtained at the beginning of the sampling event.

- Action Item: NV Energy to provide tables of analytical results from August sampling event when available from the laboratory.

Laser Induced Fluorescence (LIF) Investigations – Approximately 100 UVOST locations have been completed to date; though flooding has currently interrupted work in the field. Work is scheduled to resume on December 1, 2014. As outlined in the Work Plan, soil samples will be collected and analyzed to confirm and quantify the impact identified with the UVOST probes.

October 8

Points of Compliance – Possible points of compliance for the Station were discussed, including the Muddy River and the facility boundary. Potential future receptors (onsite and offsite) should also be considered. NDEP stated that the current station CSM needs to be updated prior to making any significant remedial decisions. The CSM will be updated in 2015 with data collected during implementation of the Muddy River Investigation and Pond Area Investigations, and a CSM workshop will be held with NDEP in the fourth quarter of 2015. The following CSM data gaps were discussed and will be incorporated into the preparation of the pond area characterization work plans:

- Vertical extent of groundwater contamination in the pond area
- Downgradient extent of groundwater contamination
- Vertical extent of potential secondary source material in the pond area
- Mass flux leaving Station boundary in groundwater and surface water
- Geochemical processes in soil and groundwater in the pond areas
- Plume stability (evaluation using MAROS, data trends in wells, and statistical analyses)

- Action Item: NDEP to provide list of CSM data gaps; NV Energy will use this information to address data gaps in work plans, as appropriate.

NV Energy Schedule–Next year (2015) is targeted for data collection in the evaporation ponds and Muddy River area, as well as in coordination with the demolition/decommissioning of Units 1-3. Additional investigations will be conducted in the Unit 4 areas after Unit 4 shuts down at the end of 2017. NV Energy anticipates that corrective actions will be implemented in the next 8 - 10 years.

NV Energy would like to pursue evaluation of the groundwater beneath the Mesa landfill if the Muddy Creek-Mesa background groundwater concentrations are approved by NDEP. NV Energy will submit a

memo to NDEP for review that outlines the statistical approach planned to evaluate whether the Mesa groundwater requires further investigation and/or corrective action. The Work Plans for implementation in 2015 will be submitted as follows:

Investigation Area	**Work Plan to NDEP**	**Estimated Start Dates**
Muddy River	December 2014	Field activities in February 2015
PA-2 (4B and 4C Ponds)	February 2015	April 2015
PA-3 (Former Pond 4A)	February 2015	April 2015
PA-5 (Former Pond D); PA-6 (Ponds E-1 and E-2); PA-7 (Former Ponds F and G)	February 2015	April 2015
Petroleum Source Areas	Q1 2015	Q3/Q4 2015
Units 1 – 3 Station Source Areas	Q1 2015	Q3/Q4 2015

- Action Item: NV Energy to submit memo outlining statistical approach to evaluate Mesa groundwater.

Preliminary Geochemical CSM– Brad Bessinger/SSPA made a presentation on the preliminary geochemical CSM related to the pond areas and the Muddy River based on data available to date. Once the laboratory data from the August field investigations are available, they will be integrated into the Preliminary Geochemical CSM, and a report will be submitted to NDEP in early 2015.

- Action Item: NDEP to give NV Energy comments on information they would like to see in the Preliminary Geochemical CSM Report.

Muddy River Investigation Work Plan Workshop– The group worked together to develop the following Work Plan objectives, lines of evidence, and field investigations scope:

Objectives

- Current status of Muddy River water quality – NV Energy will present to NDEP in a focused memo, as discussed in the action item under "Background" above
- Where is river gaining/losing?
- What is mass flux of TDS to river from the pond area TDS plume?
- Variations in gaining/losing portions of the river – seasonal and historic, as well as during episodic events (floods, droughts)
- Variations in water quality (same as above)
- Fill in geochemical data gaps related to groundwater/surface water interaction

Lines of Evidence

- Hydrogeology – soils, permeability, flow
- Groundwater/surface water elevations
- River geometry
- Visual evidence of seeps
- Field water quality changes in river water column

- Water quality changes in river (upstream to downstream)
- Water balance
- Microwells – optional

Field Investigations Scope

- Eleven transects across the Muddy River will be surveyed (post-flood). Locations include areas upstream, downstream and within the pond area.
- Sediment depth measurements and visual characterization of sediment materials (soils classification) completed at all 11 transects
- Install piezometers or use existing wells (both sides of river if possible) at all 11 transects
- Surface water and groundwater measurements of: elevation, pH, temperature, and conductivity(manual measurements monthly at 7 transects; dataloggers for continuous data collection at 4 locations)
- Quarterly FlowTracker flow measurements at all 11 transects – during the same day
    - one replicate measurement will be done per measurement team, per event
    - compare flow measurement values using a method that relies on one velocity measurement per location and a method that relies on two velocity measurements per location
- Quarterly south gate spring flow measurement by bucket and stopwatch method
- Dairy diversion flows from flume available hourly
- Quarterly field parameters in river-profile water column
- Visual observation of seeps – quarterly
- Surface water quality – lab samples – collect quarterly at six locations – same collection method as with past sampling
- Semi-annual groundwater sampling to be conducted at the same time as quarterly surface water events; analyze surface water for parameters to compare with groundwater parameters.

Transects – ARCADIS presented a hand-drawn/draft cross section with information on TDS concentrations that they would like to see on future transects. These types of transects could be used to estimate mass flux.

- Action Item: NDEP to provide ARCADIS's transect sketch to NV Energy.

Additional Action Items:

- NDEP review of the following submittals: Background Report, Pond E2 Work Plan, and Groundwater Monitoring Report Parameter Reduction Memo.
- NDEP to provide NV Energy comments on ARCADIS field oversight of the Muddy River Field Investigation completed in August, 2014.
- ARCADIS to provide NV Energy with Scopes Of Work for their assistance to NDEP on the review of upcoming pond area characterization Work Plans
- NV Energy to provide NDEP with excel tables of data used in the geochemistry CSM
- NV Energy to provide NDEP with the 1995 pond report referenced during the geotechnical presentation

Next AOC Meeting – The fourth quarter AOC meeting is scheduled for December 11, 2014. The time and location will be determined at a later date.

NDEP ACTION ITEMS				
Priority	**Deliverable**	**Submittal Date**	**Party Responsible**	**Notes**
1	Information to be included in Preliminary Geochemical CSM Report to NV Energy	---	NDEP/ARCADIS	
2	List of CSM data gaps to NV Energy	--	NDEP/ARCADIS	NV Energy indicate in which work plans they will be addressed
3	Provide comments and/or approval on the *Background Conditions Repor*t, Draft July 2014	8-1-14	NDEP/ARCADIS	
4	Provide comments and/or approval on the Memo Outlining Proposed Groundwater Sampling Program Changes	9-24-14	NDEP/ARCADIS	
5	Provide comments and/or approval of the Meeting minutes from April 30, 2014 quarterly AOC meeting	7-24-14	NDEP/ARCADIS	
6	Provide comments and/or approval of the *Solids Removal Work Plan Pond E-2*, Draft September 2014	9-30-14	NDEP/ARCADIS	

NEAR TERM DELIVERABLES TO BE SUBMITTED TO THE NDEP			
Deliverable	**Estimated Delivery Date**	**Party Responsible**	**Notes**
Meeting Minutes from August 18, 2014, Quarterly AOC Meeting	October 2014	NV Energy/Stanley Consultants	
Observe Muddy River banks for seeps	October 2014	NV Energy/Stanley Consultants	
Tables of laboratory data from August 2014 sampling event	November 2014	NV Energy/Stanley Consultants	
Mesa Groundwater Evaluation Approach Memo	Q4 2014	NV Energy/Stanley Consultants	
Muddy River Water Quality Memo	Q4 2014	NV Energy/Stanley Consultants	
PA-8 (H2O2 Tank Release) request for Investigation Closed (IC) status	Q4 2014	NV Energy/Stanley Consultants	
SA-12 (Former Diesel AST) request for IC status	Q4 2014	NV Energy/Stanley Consultants	
SA-17 (WMU 8 Previous Disposal Area) request for IC status	Q4 2014	NV Energy/Stanley Consultants	
Pond 4A Solids Data and Validation Reports	Q4 2014	NV Energy/Stanley Consultants	
Updated Community Relations Fact Sheet and Site Figure	Q4 2014	NV Energy/Stanley Consultants	
Muddy River Investigation Work Plan	December 2014	NV Energy/Stanley Consultants	Field work to start in February 2015
Annual Groundwater Monitoring Report	January 30, 2015	NV Energy/Stanley Consultants	
Laser Induced Fluorescence (LIF) Report	February 2015	NV Energy/Stanley Consultants	LIF work delayed due to flooding
PA-2 Soils and Groundwater Characterization Work Plan	February 2015	NV Energy/Stanley Consultants	Field work start in April 2015
PA-3 Soils and Groundwater Characterization Work Plan	February 2015	NV Energy/Stanley Consultants	Field work start in April 2015
PA-5-7 Soils and Groundwater Characterization Work Plan	February 2015	NV Energy/Stanley Consultants	Field work start in April 2015
Preliminary Geochemical CSM Report	March 2015	NV Energy/Stanley Consultants/ SSPA	
Petroleum Source Area Work Plans SA-14 and SA-15	Q1 2015	NV Energy/Stanley Consultants	Field work to start in Q3 or Q4 2015
Units 1 – 3 Station Area Work Plans SA-4, SA-8, and SA-19	Q1 2015	NV Energy/Stanley Consultants	Field work to start in Q3 or Q4 2015
Revised/additional Station geologic cross-sections	Q4 2015	NV Energy/Stanley Consultants	

NV Energy – Reid Gardner Station
Implementation of Administrative Order on Consent
Muddy River Technical Meeting and Site Visit
October 7 – 8, 2014
List of Attendees

Name	Representing	Phone	E-Mail
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Cause and Remediation of Hydrogen Sulfide Emissions from a Sodium-Based Flue Gas Desulfurization Sludge Disposal Pond

C. C. Ainsworth,* D. Rai, and S. C. Smith

ABSTRACT

A flue gas desulfurization (FGD) sludge disposal pond with a history of H_2S emissions to the atmosphere was studied to determine the cause of emissions and remediation strategies. The pond receives sludge and associated waters from a single-pass Na_2CO_3 flue gas scrubber unit. The pond water is a sodic alkaline brine with large SO_3 and S_2O_3 concentrations (>5000 mg L^{-1}), and hence, an elevated chemical O_2 demand. The pond water H_2S concentrations are small as a result of periodic H_2O_2 additions. The sediments, however, have as much as 3500 mg L^{-1} H_2S in the pore water. The production of H_2S appeared to originate from the sediments and diffuses through the anoxic water column with little oxidation. Large concentrations of the reduced sulfur species SO_3 and S_2O_3 were present as a result of the flue gas desulfurization process and incomplete oxidation of H_2S. The pond was reconstructed to circulate the water through an air injection system that was designed to oxidize the SO_3 and S_2O_3 to SO_4, and thereby reduce the chemical O_2 demand. After the installation of the air injection system, emissions of H_2S ceased and the concentrations of SO_3 and S_2O_3 were reduced by at least a factor of 10 within 3 to 4 wk. The production of H_2S in the sediments, however, did not appear to be affected, nor did it appear that it will be reduced in the future by the air injection system.

All coals contain reduced organic or inorganic S compounds. Combustion of coal to produce electricity transforms large quantities of the reduced S to sulfur dioxide [$SO_{2(g)}$]. Atmospheric release of $SO_{2(g)}$ has been linked to acid rain, which contributes to acidification of poorly buffered lakes and possibly forest decline (Gaffney et al., 1987). In order to reduce emissions of $SO_{2(g)}$ to the atmosphere, many coal-fired generating stations use postcombustion FGD scrubbing systems. These systems convert $SO_{2(g)}$ to SO_3 or SO_4. Both wet and dry desulfurization processes are currently used; however, wet techniques are most often used, and produce large quantities of nonregenerable waste (Bern, 1976; Summers et al., 1983). Wet scrubbing processes may use (i) $CaCO_3$, (ii) CaO, (iii) alkaline fly ash, and (iv) Na_2CO_3 as scrubbing material. Fresh sludge typically contains unspent scrubber material, Ca (or Na) sulfate and sulfite and a percentage of entrained fly ash.

The concentration of water-soluble constituents in Ca- and Na-based FGD sludge waters depends on the scrubbing agent, composition of the coal burned, the quantity of fly ash entrained in the flue gas scrubbing process, and the use of forced-air oxidation (Ainsworth et al., 1994a; Ainsworth and Rai, 1987; Summers et al., 1983). Unlike a Ca-based sludge where SO_3 and SO_4 are precipitated as relatively insoluble Ca solids (Ainsworth et al., 1994a,b; Rai et al., 1987, 1989), Na-based sludge waters exhibit large concentrations of SO_4 and SO_3 because of the solubility of the Na salts of these ions [$Na_2SO_4 \cdot 10\ H_2O$ (mirabilite) and $Na_2SO_3 \cdot 7\ H_2O$]. These solids precipitate in the ponds because of temperature fluctuations and water evaporation. As a result, bottom sediments tend to become sealed off from the atmosphere by overlying waters and by the precipitation of mirabilite. Continuing microbial activity below the mirabilite-precipitation zone produces reducing conditions. Under these conditions, sulfate and sulfite reduction occurs and H_2S is produced (Rai et al., 1987; Ainsworth et al., 1994b).

A coal-burning, electric-generating station using a single-pass Na_2CO_3 scrubber was studied. The station's disposal ponds receiving the scrubber materials have a history of $H_2S_{(g)}$ emissions at levels large enough to be of regulatory concern as a nuisance odor condition in the nearby community. At the time of initial sampling, periodic H_2O_2 addition to the ponds was being used as an emission abatement technique for $H_2S_{(g)}$. Even though FGD scrubbing systems are widely used throughout the world, there is a dearth of scientific literature on the geochemistry of FGD disposal ponds. Therefore, the objective of the current study was to investigate the geochemistry of a Na-based FGD disposal site to (i) develop a basic understanding of $H_2S_{(g)}$ production and emission, (ii) suggest strategies for remediation of $H_2S_{(g)}$ production and emission, and (iii) evaluate the effectiveness of an air-injector system as a $H_2S_{(g)}$ emission abatement technique. To meet these objectives, a series of field and laboratory analyses of waters and solids associated with the disposal site (i.e., FGD discharge, pond waters, and sediment pore waters) were conducted. These analyses provide a basis for understanding the biogeochemistry of these ponds and for recommendations for abatement of $H_2S_{(g)}$ emissions.

MATERIALS AND METHODS

An FGD sludge disposal site associated with a coal-fired electric power generating station in the southwestern USA was sampled between September 1989 and September 1990. During this period the station used a subbituminous coal and a single-pass Na_2CO_3 scrubber system. The waste water from the scrubber system and other waste streams was sluiced to two unlined 162 000-m^2 evaporation ponds that were subdivided for evaporation management purposes (Fig. 1). Peak power generation was during the summer months when the total flow rate to the ponds ranged between 570 to 660 L min^{-1}. Flow was diverted to a given pond dependent on the volume of discharge, time of year, and pond capacity. Typically, the influent water had a total dissolved solids concentration of $\approx$75 000 mg L^{-1}; Na was the predominant cation and sulfate, sulfite, chloride and carbonate–bicarbonate ions were the major

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Abbreviations: FGD, flue gas desulfurization; ICP, inductively coupled, plasma-atomic emission spectroscopy; DOC, dissolved organic carbon; DIC, dissolved inorganic carbon; GC, gas chromatography; TDS, total dissolved solids; XRD, x-ray diffraction.

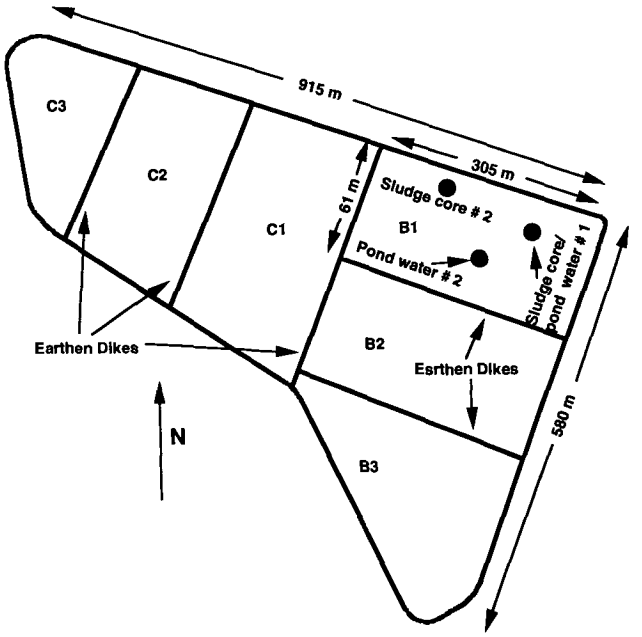

Fig. 1. Schematic of the B and C pond complex and the 1989 Pond B1 sampling locations.

anions. Other constituents included Ca, K, Mg, NO_3, and PO_4. The estimated average annual evaporation rate for the ponds was equivalent to an influent flow of 750 L min^{-1}. The ponds were constructed by simply excavating a depression in the landscape and using the natural clays present in the soil as the pond bottom. At the time of sampling, only the B1 pond was actively receiving scrubber water and required periodic additions of H_2O_2 to control $H_2S_{(g)}$ emissions. All six ponds, however, had a history of $H_2S_{(g)}$ emissions.

Water samples were collected from the bottom (at or near the water–sediment interface), at mid-depth, and at the surface. Water from the desired depth was pumped (at 2 L min^{-1}) for ≈ 5 min before sampling and preserved as described below for analyses of cations and anions. Water samples also were collected for purgeable and acid-volatile H_2S in gas sample vials; the vials were fitted with a septum and Teflon stopcock on each end. At each water sampling location, Eh (relative to the standard H electrode) and pH were measured using platinum and pH combination electrodes sealed in rigid plastic pipe with the tips protruding from the pipe end; the pipe end was placed at a desired depth and the pH and mV readings recorded by a pH/mV meter after stabilizing (usually 3 to 5 min; Rai et al., 1989). Although accurate measurement of Eh and pH in these highly concentrated brines cannot be made directly, these results can be used for qualitative comparisons across sampling locations and over time, as well as for general indicators of acidity or basicity, and oxidized or reduced conditions.

Sediment cores were removed by using a finned, 76-cm-long steel lake sediment sampler, with a lexan liner and eggshell core catcher inside the steel core barrel. The corer was dropped into the sediment and then driven to its 76-cm length. The cores were capped at both ends, sealed, labeled, and stored on ice.

Site Descriptions

September 1989 Sampling

The B1 pond water was between 40- to 80-cm deep, and had a maximum of 0.99 mg m^{-3} H_2S ambient air concentration as measured by a portable H_2S gas monitor. The B1 pond (as well as all of the other ponds) had a very hard, thick (≈ 13 cm), translucent crust on the bottom that appeared to be Na_2SO_4; a black sediment was present underneath the crust. It was not always possible to collect samples of the crust or the sediments below the crust because of the density of the crust material; however, sediment cores were removed from two locations in Pond B1 (Fig. 1). Core 1 consisted of both the crust and the underlying sediment, and was divided into an upper section (crust material) and lower section. Core 2 consisted only of the sediment. Pond waters were sampled from the two locations and Eh and pH measurements were taken at ≈ 10 locations. The plant personnel periodically added H_2O_2 to the ponds as an $H_2S_{(g)}$ emission abatement measure whenever an increase in the aqueous concentration of total sulfide was observed. For instance, the C2 pond had received 4540 L of 30% H_2O_2 2 d prior to sampling; the B1 pond, however, had not received H_2O_2 for ≈ 7 d prior to sampling.

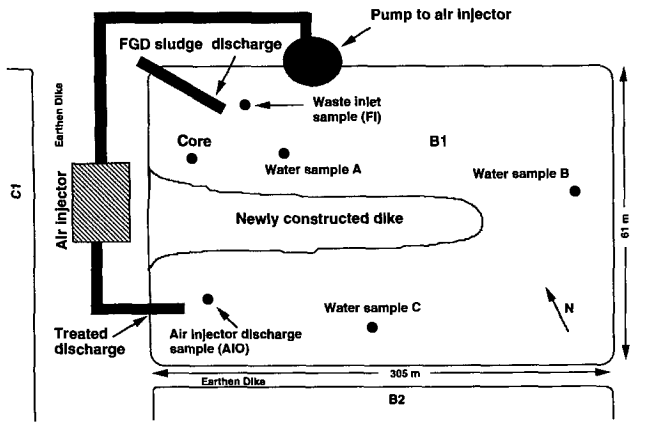

Fig. 2. Schematic of B1 pond, redesigned, fitted with a forced air oxidation system, and the 1990 sampling locations.

September 1990 Sampling

After analysis of samples collected in 1989, a causal relationship between pond water chemistry and $H_2S_{(g)}$ production and emission was hypothesized. The generating station implemented an $H_2S_{(g)}$ abatement plan for Pond B1 during the summer of 1990. This pond was reconfigured for better circulation and a forced-air oxidation system was installed (Fig 2). After the oxidation system had been in use for ≈ 3 wk, the B1 pond waters and sediments were sampled in a manner similar to that described above. Ambient air concentrations of $H_2S_{(g)}$ were less than the detection limit of the portable H_2S gas analyzer (0.07 mg m^{-3}). Unlike the 1989 sampling, the crust at the bottom of the pond could not be penetrated; only a single sediment core was collected from an area that was void of the crust. Surface and bottom water samples were collected at three locations in B1 and single samples collected near the FGD sludge discharge (sludge pond inlet) and the air injector discharge (Fig. 2).

Sample Preparation and Analyses

Water Extraction and Sample Preparation

Pore waters from the sediments in the lexan core liner were extracted by attaching it to a filtration apparatus fitted with a 18-Å cellulose filter. After the filtration system was attached, pressurized $N_{2(g)}$ was applied to the filtration system to force the interstitial water out of the sediment and through the filter.

The first 10 mL fraction of extracted solution was collected directly into a graduated cylinder containing 10 mL of sulfide antioxidant buffer (SAOB; 200 mL of 10 *M* NaOH, 35 g ascorbic acid, 67 g disodium EDTA made up to 1 L with deionized water) for sulfide measurement by ion selective electrode (ISE; Orion Research, Cambridge, MS). The ISE was used to determine the sulfide (S^{2-}) concentration in all 1989 samples and sediment pore waters from 1990 samples. Selected water samples were diluted and reanalyzed for S^{2-} concentration to delineate the influence of high ionic strength on the analytical determination of S^{2-} by ISE. The remaining pore water filtrate was collected and subsampled for chemical analysis as described below. Pore water extraction and sample preparation were performed on site and with as little time between sampling and preparation as possible; usually <4 h.

Following collection, pond water samples were filtered through a 0.22-μm Millex GS filter (Millipore, Bedford, MA) that was fitted to a 20-mL syringe or a $N_{2(g)}$ pressure filtration apparatus. The first 5 mL of filtrate were discarded prior to collecting samples for analysis. A 5 to 7 mL sample for sulfite (SO_3), thiosulfate (S_2O_3), and thiocyanate (SCN) was preserved with formaldehyde (10 μL of 3.7% formaldehyde mL^{-1}). A similar amount of filtered solution was acidified with concentrated, ultrapure HCl (10 μL HCl 3 mL^{-1}) for determination of cation concentrations. A 30-mL sample of unacidified filtrate was placed in a polypropylene bottle for the determination of anions other than the aforementioned S species.

Laboratory Analyses

The concentrations of SO_3, S_2O_3, and SCN were determined by ion chromatography (IC) from a subsample preserved with formaldehyde. The concentrations of Br, Cl, F, I, MoO_4, NO_2, NO_3, PO_4, and SO_4 were also determined by IC on unpreserved samples; NO_2 and NO_3 were only determined on the 1989 samples. The IC analyses were performed using a bicarbonate eluent (1.75 m*M* $NaHCO_3$ and 1.85 m*M* Na_2CO_3) and conductivity detection. Ion selective electrode techniques were utilized to quantify the concentrations of F and NH_4. A multielement inductively coupled, plasma-atomic emission spectroscopy (ICP) was used to determine the aqueous concentrations of Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mo, Na, Ni, Pb, Sb, Si, Sr, V, and Zn. Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) concentrations were determined using a Dohrmann DC-80 C analyzer (Santa Clara, CA) with an infrared detector. Arsenic and Se redox speciation and quantification were accomplished using a hydride-reduction technique and analysis by graphite furnace/atomic absorption spectroscopy (Cutter, 1986; Crecelius et al., 1986). The pond water samples collected in the gas collection tubes were analyzed for purgeable, acid-volatile, and total H_2S by gas chromatography (GC; Cutter and Oatts, 1987). With the exception of the DOC and GC-H_2S analyses, the samples required between 100- and 1000-fold dilutions prior to determination. Dilution was required because of the large concentrations of SO_4 and Na present in the samples. As a result, concentrations of many constituents were at or below detection limits.

Proton-induced x-ray emission spectroscopy was used to determine the total elemental concentrations of Al, As, Ba, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, V, and Zn in the FGD sludge pond sediment and crust solids. All solids for this analysis were freeze-dried and then ground to pass a 44-μm sieve. XRD analysis of the crust material was performed on random mounted specimens using an automated GE/Diano 8530 diffractometer (Diano, Woburn, MA) equipped with graphite monochromator, with operation and data reduction performed by personal computer. Powdered samples were pressed into recessed holders as semirandom mounts and a diffractogram was collected.

Computer Modeling

A computer code (GMIN) based on constrained minimization of the Gibb's free energy (Felmy, 1990) was used to model the aqueous concentrations of selected chemical constituents of the Na-based FGD ponds. This code was used because it contains an aqueous ion interaction model (Pitzer, 1973, 1979) that is accurate in relatively concentrated salt solutions, and because it contains most of the necessary ion interaction parameters for the Na-SO_4 system. Calculations using this code allowed for the indirect identification of possible solubility-controlling solid phases.

RESULTS AND DISCUSSION

1989 Analysis

Solid Phase Analysis

The major constituents of the crust material were Na and S (Core 1 crust; Table 1); Si, P, Cl, and Al were minor constituents. The crust was determined, by XRD, to be $Na_2SO_4 \cdot 10\ H_2O$ (mirabilite) precipitate, and the minor element constituents were concluded to be minor debris (undetermined). The Na_2SO_4 was the major component of the sludge disposed to the pond from the single pass Na_2CO_3 scrubber; the sludge entered the pond at elevated temperatures, and as a result of the cooling and water evaporation mirabilite precipitated. Trace metal concentrations (Cd, Co, Cr, Cu, Ni, Pb, V, and Zn) were near or below detection limits in all the core samples. The small trace metal concentrations suggested that there was

Table 1. Total chemical composition of FGD solid samples from the B1 disposal pond; sampled September 1989.

Element	Core 1† Crust	Core 1 sediment	Core 2
	mg kg^{-1}		
Al	2 320	2 100	3 050
As	<5	8	7
Ba	<400	<400	<400
Br	32	15	24
Ca	404	207 000	263 000
Cd	<40	<40	<40
Cl	3 320	5 470	6 900
Co	<50	<50	<50
Cr	<25	<25	<25
Cu	19	11	12
Fe	317	443	752
K	661	<250	<362
Mg	<650	16 000	14 200
Mn	<16	17	<32
Mo	<12	12	<12
Na	220 000	77 100	93 600
Ni	<12	<12	<12
P	983	2 330	2 330
Pb	<5	12	16
S	196 000	64 100	65 900
Sb	<90	<90	<90
Se	<4	<4	<4
Si	2 210	10 800	13 400
Sn	<80	<80	<80
V	<25	<25	<25
Zn	9	17	23

† Core 1 sampled from pond 4B1 was divided into two distinct components. Crust core material (≈ 13 cm) was shown to be mirabilite. The sediment core (≈ 37 cm) was the material directly below the crust.

not a significant amount of coal fly ash entrained in the scrubber sludge water. The major constituents of Core 1 (sediment) and Core 2 were considerably different from the crust material; Ca was the dominant cation in all noncrust material (Table 1). In addition to Ca, noncrust solids contained large amounts of Al, Cl, Fe, P, Mg, Na, S, and Si. The lower black sediments appeared to be a mixture of secondary precipitates and highly reduced soil materials. The large Ca concentrations observed in the sediment cores appeared to be due to the presence of $CaSO_4 \cdot 0.5\ H_2O$ (gypsum) in the soil that made up the bottom of the pond.

Pond and Pore Water Characterization

The concentration of dissolved solids in the B1 waters was extremely large (Table 2). The total dissolved solids (TDS) concentration of all the waters was >200 000 mg L^{-1}; the major constituents were SO_4, Na, Cl, SO_3, S_2O_3, and K. Large amounts of DOC and other nutrients (NO_3, PO_4, and K) were also present in the pond and pore waters (Table 2). The pond and pore water of B1 (and the other ponds at the station) are complex brines and similar to other evaporite systems with multiple components (Harvie et al., 1980, 1984; Moller, 1988).

The total sulfide concentration was small throughout the water column but did increase with depth (Table 2). In contrast, pore water sulfide concentrations in the crust and sediments were much higher; 19.1 mg L^{-1} in the crust, 3,460 mg L^{-1} below the crust, and 1,730 mg L^{-1} in the sediment without crust. The pore water S_2O_3 concentrations in the cores were similar to the pond water concentrations (>5000 mg L^{-1}; Table 2), with the exception of the pore water from beneath the crust (1340 mg L^{-1}). The SO_3 concentrations in the pond water and pore water of the crust material, and the sediments without overlaying crust ranged between 2220 and 4760 mg L^{-1}, but the SO_3 concentration in the pore water below the crust was less than detection limits (Table 2). The concentration of trace metals (Cd, Cu, Fe, Ni, Pb, and Zn) were less than detection limits in both the pond and pore waters; with the levels of S^{2-} measured and the alkaline pH levels in all the waters, it was expected that these metals would precipitate as sulfide solids.

Large concentrations of S_2O_3 in the pond waters may indicate the incomplete oxidation of S^{2-} by O_2 or by H_2O_2 (Boulegue and Michard, 1979; Chen and Morris, 1972). Periodic $H_2S_{(g)}$ emission abatement using H_2O_2 was used depending on the aqueous S^{2-} concentration in the pond water. Dissolved H_2S levels in Pond B1 varied greatly over time as did the need for H_2O_2 treatments. Additions of H_2O_2 were not required on a daily basis, but when it was required, large volumes (350 to 4600 L) of 30% H_2O_2 were used repeatedly over several days. For example, it was not uncommon for the dissolved H_2S concentration to increase from less than detection limits to >150 mg L^{-1} during a 24-h period. Although SO_3 may also result from partial oxidation of sulfide, the bulk of the SO_3 present in the water was probably the result of the scrubbing process only; Pond B1 continually received scrubber sludge and associated waters and hence, a continual supply of SO_3. Therefore, despite the addition of large quantities of H_2O_2, a continual supply of reduced S species were produced or added to the pond. These processes kept the concentration of reduced sulfur species large and the chemical O_2 demand of the water elevated.

Geochemical Modeling

Although the measured pH values were not accurate because of very large salt concentrations, the values were

Table 2. Chemical composition of 4B1† pond and pore waters sampled in September 1989.

	Pond water			Pore water		
				Core 1		Core 2
Element-species	surface	middle	bottom	crust	sediment	sediment
	mg L^{-1}					
			Sulfur species			
S^{2-}	0.7	1.3	2.6	19.1	3 460	1 730
SO_3^{2-}	4 330	2 220	3 120	4 760	<250	3 920
SO_4^{2-}	128 300	127 200	132 700	123 700	162 270	136 970
$S_2O_3^{2-}$	6 300	6 490	7 350	5 110	1 340	5 170
SCN^-	<50	<50	<50	<50	100	70
			Other constituents			
Na	54 000	61 000	54 800	108 000	92 800	80 000
Cl	11 000	8 030	15 100	5 730	5 620	5 440
NO_3	1 600	1 620	<100	1 340	1 370	1 350
PO_4	<30	280	240	2 300	2 570	<30
B	216	192	224	272	170	160
F	510	470	320	340	400	380
K	650	640	698	850	490	540
Mg	38	34	40	46	38	<6
Ca	22	20	22	30	18	140
Si	5	4	2	8	2	3
			Other parameters			
DOC‡	159	139	155	917	476	357
pH	9.7	9.7	9.7	ND	9.1	ND
Eh (mV)	−250	−225	−234	ND	−305	ND

† Al, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, and Zn were at or less than detection limits; ND = not determined.
‡ DOC, dissolved organic carbon.

>9.0 indicating that nearly all of the measured S(VI) should have been the SO_4^{2-} species. With the assumption that SO_4^{2-} was the only S^{6+} species, calculations using GMIN were made to determine the solubility-controlling sulfate and sulfite solids. All pond waters were calculated to be in equilibrium with respect to mirabilite; X-ray diffraction analysis of the crust material showed the presence of only mirabilite. The GMIN modeling results suggested that Ca was in equilibrium with $CaSO_3 \cdot 0.5 H_2O$ in waters with large SO_3 concentrations.

Hydrogen Sulfide Generation, Emissions, and Remediation

While no enumeration of the sulfate-reducing organisms from B1 pond waters and sediments was performed, the original material deposited in these ponds contains large quantities of SO_4 and SO_3, but not S^{2-}. Therefore, $H_2S_{(g)}$ generation in the large quantities observed at this site can only come from dissimulatory SO_4 reduction by SO_4-reducers. These organisms are ubiquitous in the environment. Even though they are strict anaerobes, they can be isolated from almost any soil and become active if the proper anaerobic conditions are present (Postgate, 1984; Zinder and Brock, 1978). Given a system devoid of O_2, sulfate-reducing bacteria can maintain growth and respiration under extreme environmental conditions of temperature, salinity, and pressure (Postgate, 1984). The SO_4-reducing organisms most likely were active in the pond sediments (below the crust material). There were ample nutrients (P, K, N, and DOC) and SO_4 in the pore waters to meet the nutritional requirements of these organisms and to continually produce S^{2-}.

The largest sulfide concentrations occurred in the sediments, and specifically below the mirabilite crust. These sediments were therefore the most probable location for SO_4-reducing organisms to reside and produce H_2S. The large variations in B1 pond water S^{2-} concentrations during a 24-h period observed by daily laboratory analysis indicated that a rapid release of H_2S occurred periodically. The likely cause for the periodicity of H_2S release was that the crust trapped the H_2S produced in the sediments (note the difference in S^{2-} concentration between the sediment of Core 1 and Core 2 Pond B1 in Table 2), the concentration increased over time, and then was released through cracks. Areas of incomplete crust coverage probably acted as continual sources of H_2S to the waters above. The pond waters were anoxic and shallow, which allows diffusion of H_2S through the water column with little oxidation. The anoxic conditions of the pond waters were promoted because of the presence of SO_3 and S_2O_3 that acted as O_2 scrubbers keeping the chemical O_2 demand of the waters elevated. Incomplete oxidation of S^{2-} is very likely the major source of S_2O_3 in the pond water and sediments (Chen and Morris, 1972). The solubility of gases, such as O_2 and H_2S, decreases with increasing temperature and salt concentration, which in turn would facilitate $H_2S_{(g)}$ release to the atmosphere, especially during hot summer months (Cramer, 1982; Barrett et al., 1988).

The keys to controlling H_2S emissions to the atmosphere in the pond under study (and for that matter any of the six ponds) are to (i) reduce the chemical O_2 demand of the pond waters (i.e., reduce the levels of SO_3 and S_2O_3) and (ii) increase the depth of oxic water overlying the sediments. Although the data collected did not show the speciation of sulfide in the pond waters to be important, alkaline conditions should be maintained to ensure that the dominant sulfide species are HS^- or S^{2-} because oxidation of H_2S by O_2 is considerably slower than for the other sulfide species (Buisman et al., 1990).

1990 Analysis

In 1990, Pond B1 was redesigned and fitted with a forced air oxidation system designed to oxidize the SO_3 to SO_4 in the newly disposed sludge, and recirculate the B1 pond waters through the air injector system to reduce the chemical O_2 demand (a schematic of the redesigned pond is shown in Fig. 2). Also, the water level was increased to 120 cm. After the installation of the air injection system, Pond B1 did not experience large fluctuations in S^{2-} concentrations or $H_2S_{(g)}$ emissions to the atmosphere.

Pore and Pond Water Analysis

Since the previous sampling, the crust overlying the pond sediments had become impenetrable. In addition, the water just above the crust was more turbid than the rest of the water column. The only location where a sediment core could be taken was from an area void of the crust material. Surface and bottom waters were sampled in five locations throughout the pond including bottom waters near the fresh FGD sludge discharge pipe (Sample FI) and the air injector discharge (sample AIO). Unlike the previous site visit, no $H_2S_{(g)}$ odor was noted, nor had any H_2O_2 additions to the pond been required since it had been reengineered.

The chemical composition of the surface pond water, regardless of where the samples were collected, was still dominated by SO_4, Na, Cl, K, and a TDS level similar to that observed in 1989. The major difference was in the SO_3 and S_2O_3 species, which were well below the 1989 levels (Tables 2 and 3). All reduced S species in the surface waters were near or at detection limits (Table 3). The composition of the bottom waters was about the same as the composition of the surface waters except with respect to total H_2S and S_2O_3 concentrations (Table 3). Although SO_3 concentrations were at or near the detection limits at all sample locations, S_2O_3 concentrations varied substantially between the FI and AIO locations (Table 3); in all cases, however, S_2O_3 concentrations were considerably smaller (less than or equal to a factor of 10) than the levels observed in 1989 (Tables 2 and 3).

The pond water sulfide data reported for 1990 (Table 3) were the result of GC determinations; data for 1989 (Table 2) were determined by ISE measurements. As seen in Table 4, ISE measurements substantially underestimated the total sulfide concentrations in the pond bottom waters. At small S^{2-} concentrations, the ISE measurement was accurate. At large concentrations, however, ISE measurements underestimated total H_2S (Table 4).

Table 3. Chemical composition of B1† pond and pore water sampled in September 1990 after the forced air oxidation system had been operating for ≈3 wk.

Element-Species	Pond water: Site A surface	Site A bottom	FI	AIO	Pore water‡
	mg L^{-1}				
	Sulfur species				
S^{2-}/H_2S	0.02	375	263	<0.3	1 730
SO_3^{2-}	<250	<250	<250	<250	2 370
SO_4^{2-}	94 870	115 240	152 340	122 120	117 030
$S_2O_3^{2-}$	<250	350	700	<250	1 194
	Other constituents				
Na	37 900	40 700	57 400	74 000	68 100
Cl	9 880	11 760	24 700	12 000	10 520
B	160	170	130	305	270
F	118	121	128	128	21.4
K	800	770	720	790	1 200
Mg	67	20	71	126	<6
Ca	38	38	23	68	26
Si	2	1	1	4	1
	Other parameters				
DOC	15.5	17.7	21.5	18.6	429
pH	9.3	9.3	9.5	9.2	8.9
Eh (mV)	15	−200	−328	−25	−465

† Al, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, and Zn were at or less than detection limits.
‡ Pore water samples were determined by ion selective electrode (S^{2-}), the pond water samples were determined by gas chromatography (H_2S).

There was a small amount of the total H_2S (≈2 to 11.4%) present in the pond waters as the nondisassociated acid (H_2S, measured as purgeable H_2S). This would suggest that the pH was about 1 to 2 pH units above the pK_{a1} of H_2S. All pore water sulfide determinations for 1989 as well as 1990 were performed with the ISE. As previously discussed, however, 1989 determinations of S^{2-} by ISE were unaffected by the large salt concentrations. If a similar fraction of the total sulfide in the pore water is in the volatile H_2S form, then the extremely large levels of S^{2-} observed in the sediment waters may be underestimated by as much as 100 to 500 mg L^{-1}. In addition, the rate of sulfide oxidation by O_2 is slower for H_2S than for the ionized species HS^- and S^{2-} (Buisman et al., 1990). Despite the presence of H_2S, however, no significant emissions of $H_2S_{(g)}$ to the atmosphere have been noted since the air injector has been on line. This would suggest that the water column was deep enough and O_2 was present in large enough concentrations to oxidize any H_2S in the upper part of the water column.

Table 4. Comparison of sulfide analyses of B1 pond bottom water sampled during September 1990.

Sulfur species	Surface water	Bottom water: A	C	FI	AIO
	mg L^{-1}				
S^{2-}(ISE)	0.02	126	18	98	0.02
Gas chromatography					
H_2S Purgeable†	<0.3	30.5	35.5	5.8	<0.3
H_2S Acid Volatile	<0.3	314	297	234	<0.3
H_2S Total	<0.3	375	311	263	<0.3

† Purgeable fraction determined by cold-trap collection by He gas, followed by injection into gas chromatography. Acid volatile fraction determined by acidification of sample in a closed chamber to about pH 2 after the purgeable fraction was determined. Total H_2S determined on nonpurged sample that was treated by acid-volatile technique.

The AIO water was clearly affected by the air injection system, and contained less reduced S species and was more oxidized. This was believed to be primarily the result of the chemical oxidation of reduced S species, promoted by oxygenation of the discharge waters and physical turbulence near the discharge site. These actions kept the waters oxic and appeared to result in the oxidation of any H_2S generated from the sediments. These effects, however, were localized to a small area around the AIO sample location, and air injector discharge point as can be seen by the H_2S and S_2O_3 concentrations at locations AIO, C, A, and FI (Tables 3 and 4; Fig. 2). While H_2S was present in the bottom waters away from the AIO location, the chemical O_2 demand had been lessened sufficiently such that the H_2S was confined to the deeper waters and was apparently oxidized as it was dispersed throughout the water column. While the presence of S_2O_3 in the bottom waters away from the air injector discharge point indicated incomplete H_2S oxidation occurred, the surface water concentration was below detection suggesting that the pond depth and oxic conditions were sufficient for complete oxidation of reduced S species. The construction of the dike and the positioning of the FI and AIO on opposite sides of the dike created a counterclockwise movement of water, and a continual mixing motion that may have aided in the dispersion of H_2S diffusing up from the sediments.

The chemical composition of the pore water appeared unaffected by the reconstruction of pond B1. The comparison of pore water chemistry was based on the results from cores collected in areas where no crust was present (Tables 2 and 3). Although there was a nearly five-fold decrease in the S_2O_3 concentration in the sediments, there was a minimal decrease in the SO_3 concentration and no apparent decrease in the S^{2-} concentration when compared with the 1989 data. The change in S_2O_3 concentration was probably the result of diffusion out of the sediments and minimal production of S_2O_3 after the startup of the air injection system. The minimal change in SO_3 concentration in the sediment pore waters, on the other hand, may have been the result of the presence of $Na_2SO_3 \cdot 7\ H_2O$ in the sediments acting as a source of SO_3. If this is the case, the SO_3 concentration should decline with time as the $Na_2SO_3 \cdot 7\ H_2O$ dissolves because the original source of the SO_3 has been removed by forced-air oxidation. Although concentrations of other reduced S forms in the pore waters should decline, there is no expectation that dissimulatory SO_4 reduction will stop or presumably decrease substantially. Therefore, it was not believed that sediment H_2S levels (particularly below the crust) will be greatly impacted by the system presently employed.

SUMMARY AND CONCLUSIONS

The large Na and SO_4 concentrations observed at the study site significantly affected the analysis of the aqueous constituents, and illustrate the difficulty of working in brine systems. Of particular interest was the quantification of sulfide by gas chromatography when compared with ISE. Although the large salt concentrations did

not appear to affect the ISE measurement, comparisons between the 1990 GC and ISE sulfide determinations were variable and demonstrated the loss of $H_2S_{(g)}$ even when the sample was placed directly into the antioxidant buffer.

The effect of air injection on pond water geochemistry was demonstrated by a comparison of water analyses from pre- and post-air injector operation. While the total dissolved solids and the principal aqueous species (Na, SO_4, Cl, and K) had not changed, the reduced sulfur species (SO_3 and S_2O_3) decreased by more than a factor of 10 throughout the pond. In addition, the DOC content had also decreased by about the same factor. Although sulfide was still being produced (as evidenced by the S^{2-} concentrations observed in the 1990 bottom water), the chemical O_2 demand of the pond waters had been substantially reduced. In addition, emissions of H_2S to the atmosphere had ceased.

The pore water from cores exhibited almost no change in composition as a result of air injection; only S_2O_3 concentrations had decreased but were still large. Because S_2O_3 production in the overlying waters had been reduced, the S_2O_3 decrease was probably caused by diffusion out of the sediments. Total H_2S concentration in the pore water has not significantly changed, suggesting that H_2S production in the sediments was fairly constant, as was its release to the overlying pond water in areas without the mirabilite crust. This suggests that (i) the sediments are, to date, not greatly affected by the air injection process, (ii) decrease of reduced S species concentrations in the sediments will be slow in areas without crust, (iii) in those areas where the crust is present, decrease of reduced S species concentrations will be extremely slow, if it occurs at all, and (iv) it is unlikely that the air injection system will affect the H_2S production in the sediments.

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