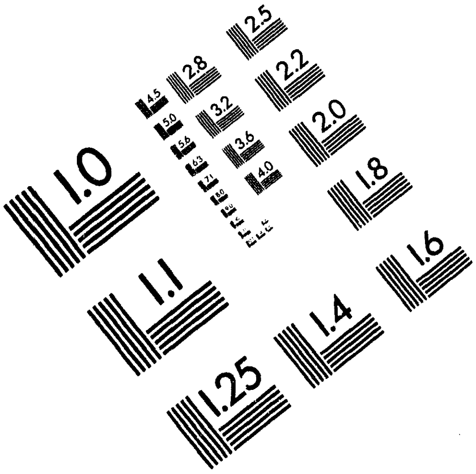

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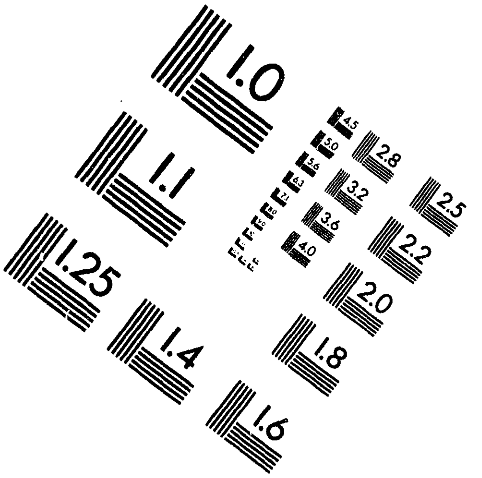

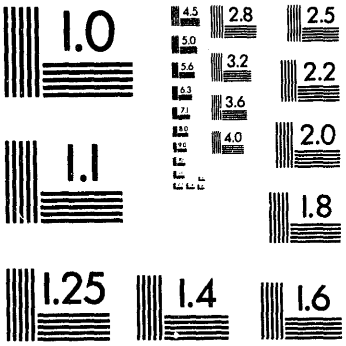

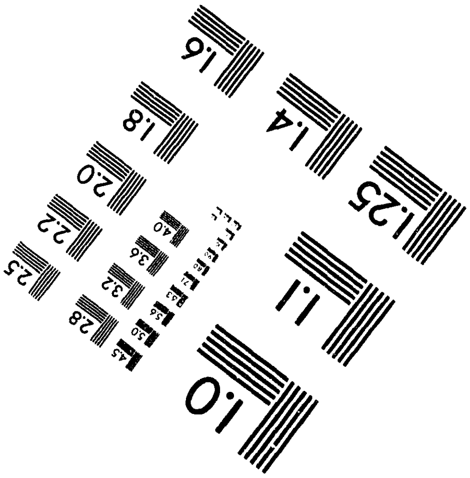

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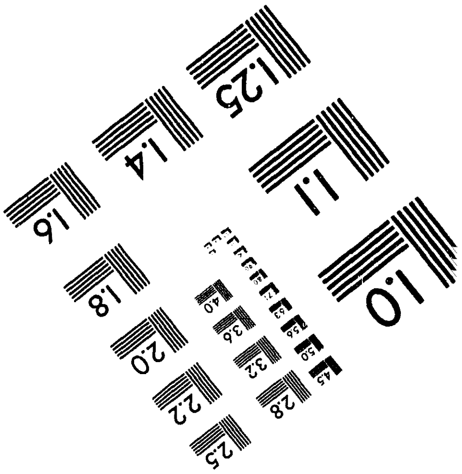


1 of 1

CHEMICAL PRE-TREATMENT OF WASTE WATER FROM THE MORCINEK MINE IN POLAND

William Bourcier
Kenneth J. Jackson

Lawrence Livermore National Laboratory

Table of Contents

SUMMARY

This report presents a treatment strategy for brine that is recovered from the Morcinek mine near the city of Kartowice in Upper Silesia, Poland. The purpose of the study is to provide sufficient chemical composition and solubility data to permit selection of equipment for a pilot scale waste water processing plant. The report delineates: 1) the pre-treatment steps necessary before the brine is delivered to a reverse osmosis unit; 2) the composition of the brine solution at various stages in the pre-treatment process and during the reverse osmosis step; 3) the types and amounts of chemicals that need to be added to the brine during pre-treatment. Analysis of the composition of the brine slurry from the submerged combustion evaporator that follows the reverse osmosis unit and the composition of brine elements that might be carried into the exhaust stack of the evaporator will be dealt with later.

The pre-treatment process will consist of four steps: (1) aeration and addition of sodium carbonate, (2) multimedia filtration, (3) addition of hydrochloric acid, and (4) ultrafiltration. On the basis of one m^3 of the brine that has a density of 1.03 g/cm^3, approximately 800 grams (1.7 lbs.) of sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$) and 60 grams (0.12 lbs.) of concentrated hydrochloric acid (HCl) will need to be added to the brine during pre-treatment. During the pre-treatment process, our calculations predict that the concentration of Ca will decrease from 1170 to 906 ppm, Mg from 460 to 442 ppm, Sr from 42 to 2.3 ppm, and Ba from 2 to 0.05 ppm. These decreases in concentration are sufficient to prevent later precipitation of inorganic solids in the reverse osmosis unit. The concentrations of Al, Fe, and other metals potentially harmful to the reverse osmosis membrane will also decrease to low levels during the pre-treatment process where they are not expected to be a problem. Filtration will be used to remove chemical precipitates after the addition of sodium carbonate and before the addition of HCl. Ultrafiltration to remove particles (such as colloids) larger than about 0.1 microns should also be performed before the brine passes into the reverse osmosis unit. The fluid entering the reverse osmosis unit has a salt concentration of 30,700 ppm. The reverse osmosis unit will separate the brine into a stream of potable water with a salt concentration of 500 ppm and a stream with a salt content of 70,000 ppm.

The exhaust from the submerged combustion chamber will consist primarily of water and carbon dioxide with minor and trace amounts of hydrocarbons. More detailed predictions of exhaust gas composition depend on our analysis of trace organics in the mine waters which is not yet complete.

The goal of the pre-treatment is to produce a fluid that is always undersaturated with respect to all mineral phases. However, only the minimum amount of pre-treatment chemicals should be added in order to minimize costs. Therefore the overall

goal is to generate a fluid that approaches but does not exceed saturation at the end of the reverse osmosis process. The suggested amounts of chemicals reported here are therefore the minimum amounts that need to be added during pre-treatment to keep all salts in solution during the reverse osmosis process.

SAMPLE COLLECTION

The Morcinek coal mine produces about 6000 metric tons/day of coal from strata at three levels (~ 600 meters deep). Waters produced from the Morcinek mine commingle before being pumped to the surface for discharge in an approximately 50x25x5 meter lined concrete settling pond where the total suspended load is reduced from 70 to 30 mg/liter (see Figure 1). The fluid discharge temperature was approximately 22°C while the fluid in the settling pond was at 12°C during the November sampling. A second pond (25x25x5 meters) is currently under repair and will be available for the pre-treatment process. Currently the mine waters are discharged in a nearby river without further treatment. The expected changes in chemical composition of the brine over time are currently unknown. However, the results of periodic sulfate and chloride analyses of the mine waters have not changed much over the last couple years.

Brine samples were collected from input and discharge ends of the settling pond. Care was taken in sampling to insure that gases did not escape and that precipitation of solid phases did not occur after sampling. Samples were taken in high density polyethylene bottles for cation analysis, and in glass bottles (with Teflon-lined lids) for analysis of dissolved organics and gases. A detailed sampling procedure is presented in Appendix 2 of this report. During residence in the pond, the concentrations of dissolved species in the mine waters change little (see Table 1). These chemical changes can be accounted for by consideration of temperature changes, mineral precipitation, sorption onto precipitated and suspended solids, and settling out of particulates.

SAMPLE ANALYSIS

Cations were analyzed using either atomic emission spectroscopy (AES), inductively coupled plasma emission spectroscopy (ICP-AES), or inductively coupled plasma mass spectroscopy (ICP-MS). AES provides a qualitative and inexpensive analysis of most elements and is used to determine the major and minor chemical components of the fluid. ICP-AES provides a quantitative analysis of most cations and was used

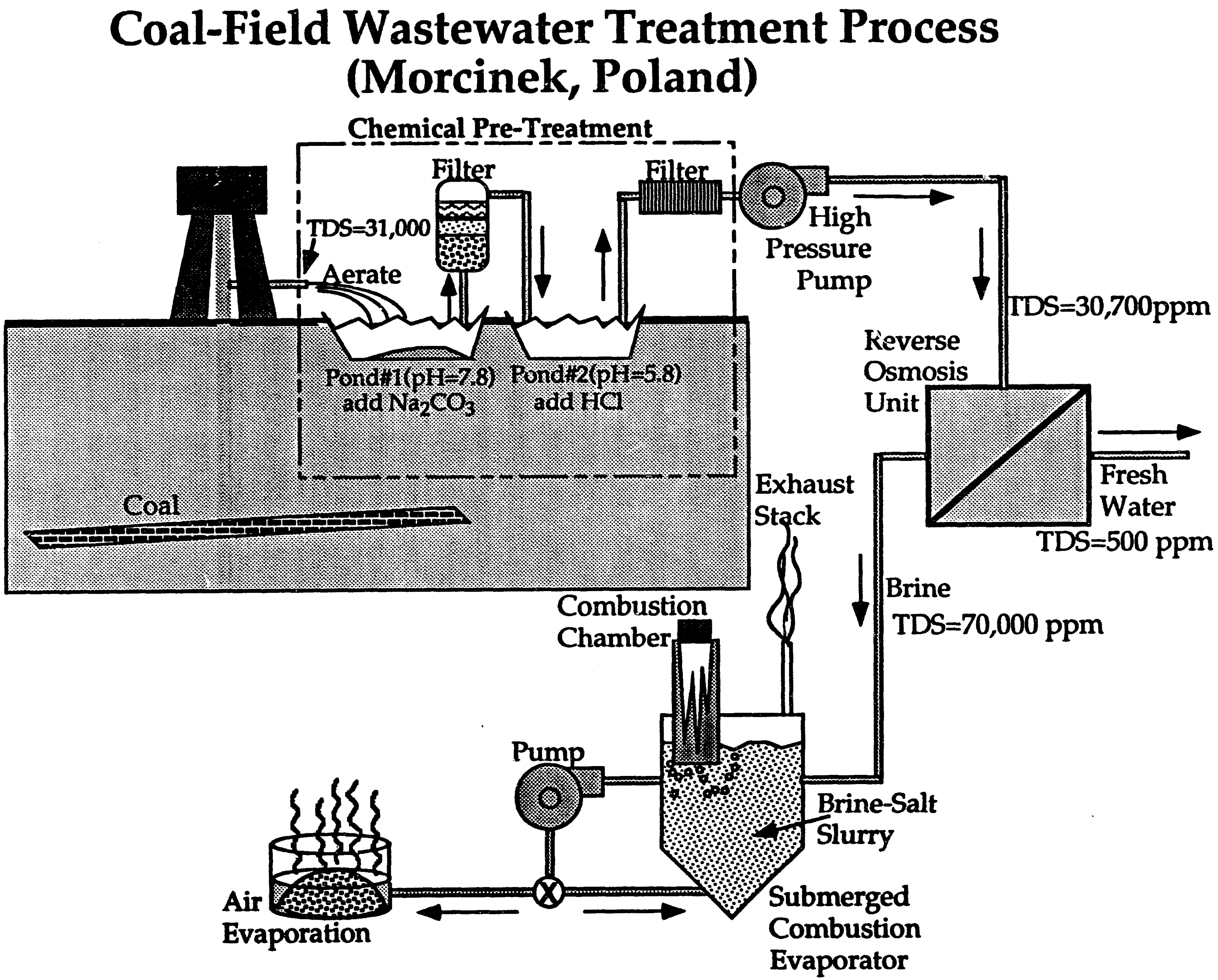


Figure 1. Schematic of Morcinek coal-field wastewater treatment process.

for most of the brine components. It also provides total sulfur and total phosphorous analyses. ICP-MS provides a quantitative analysis which is optimum for heavy metals at low concentrations. Anions were determined using ion chromatography (IC) and liquid chromatography (HPLC). Volatile organic hydrocarbons (VOCs) were analyzed using gas chromatography (results not included in this report).

The unfiltered pond samples were passed through 5 micron filters in the laboratory before being analyzed. The solids captured during filtration were also analyzed (see Table 2).

ANALYTICAL RESULTS

Table 1 shows the analytical results for the Morcinek samples for both the inlet and discharge sides of the settling pond. Relatively minor changes in dissolved species concentrations are observed across the pond. However, the suspended solids load decreases by about 50% due to settling out of the suspended load. The waters, which have a TDS content of about 31,000 ppm, contain appreciable concentrations of elements potentially harmful to the reverse osmosis membrane material including Ca, Mg, Ba, Sr, with much lesser amounts of Fe, Si, and Al. Calculations of the saturation state of the mine water as it leaves the mine shows that the water is near or exceeds saturation with respect to several iron and manganese oxide phases, clays, and several carbonate and sulfate phases. The concentration of calcium is particularly high (1100 ppm) relative to other elements and is the element most likely to cause scaling problems in the reverse osmosis unit. An approximately 30% increase in concentrations of the dissolved species in the water during reverse osmosis treatment will further increase the supersaturation of these mineral phases. Our pre-treatment process is aimed at reducing the amounts of these elements in the mine water prior to reverse osmosis treatment, to levels where, even after treatment, no mineral phases will be supersaturated and have the potential to precipitate in the RO membrane.

Table 2 shows the composition of the suspended solids filtered from the solution samples. They are dominated by barium, magnesium, and silicon with lesser amounts of aluminum, iron, potassium, manganese and strontium. The mineral phases making up the suspended load probably include carbonates and sulfates of Ca, Ba, and Mg; iron hydroxides; and clays. This will be confirmed with x-ray diffraction analysis of the materials. The concentrations of some elements, such as Al and Mn, increased in relative concentration in the filtrate (suspended load) in going from the inlet to the discharge ends of the pond. This may reflect the precipitation of solids which contain those elements during fluid transit across the pond.

The pond inlet temperature was 20°C and discharge temperature 12°C during the November sampling. Because the temperature differential across the pond will be seasonal and may be reversed in the summer, we have assumed a constant temperature of 25°C for all of our modeling calculations. The temperature effects can be explicitly accounted for later when given more specific information.

Table 1. Measured concentrations of Morcinek mine waters in mg/kg water. IN refers to samples on input end of settling pond, OUT refers to outlet (discharge) end. ND means "not detected" for the analytical method used.

ELEMENT	IN	OUT	ELEMENT	IN	OUT
Aluminum(Al)	<0.7	<0.7	Silicon(Si)	6.4	6.7
Barium(Ba)	1.2	2.1	Sodium(Na)	10,109	10,684
Boron(B)	6.3	6.7	Strontium(Sr)	40	43
Bromium(Br)	ND	ND	Sulfur(S)	85	87
Calcium(Ca)	1131	1216	Zinc(Zn)	<0.1	<0.1
Copper(Cu)	<0.1	<0.1	Bromide(Br)	ND	ND
Iron(Fe)	<0.2	<0.2	Chloride(Cl^-)	19,731	20,294
Lithium(Li)	1.2	1.3	Fluoride(F^-)	.42	NA
Magnesium(Mg)	443	470	Nitrate(NO_3^-)	31.1	28.5
Manganese(Mn)	1.1	1.1	Nitrite(NO_2^-)	2	5
Nickel(Ni)	<0.5	<0.5	Phosphate(PO_4^{3-})	ND	ND
Phosphorous(P)	7	7	Sulfate(SO_4^{2-})	252	246
Rubidium(Rb)	.23	.24	pH	7.5	7.0
Potassium(K)	140	149	Temperature(C)	20	12

PRE-TREATMENT METHODS

Subsurface fluids are typically saturated with respect to multiple mineral phases with which they are in contact (Morel and Hering, 1993). Several processes associated with production of these fluids may affect the solubilities and potentially precipitate solids from these fluids: (1) oxidation through contact with atmospheric oxygen (which precipitates elements such as iron (Fe) and manganese (Mn) which are less soluble under oxidizing conditions); (2) loss or gain of other gases, especially carbon dioxide, while the fluids are stored in the holding pond in contact with air; (3) the temperature change associated with transport of the fluids from the subsurface to the holding pond; and (4) increase in concentration of dissolved species during reverse osmosis treatment of the fluids. The increased dissolved salt content of the brine produced during the reverse osmosis process may cause precipitation of solids as they become supersaturated during the removal of water. Previous experience together with computer modeling calculations indicate that these precipitates may include calcite ($CaCO_3$), barite ($BaSO_4$), gypsum ($CaSO_4.H_2O$), celestite ($SrSO_4$), fluorite (CaF_2), silica, clays, and iron oxides (Isner and Williams, 1993), (Fountoukidis, Maroulis and Marinos-Kouris, 1990).

Table 2. Semi-quantitative analysis of suspended sediment in Morcinek mine waters sampled at inlet (IN) and discharge end (OUT) of settling pond. Measurements are in PPM by weight. ND means "not detected" for the analytical method used.

ELEMENT	IN	OUT
Calcium	>5000	>5000
Silicon	>5000	300
Magnesium	>5000	>5000
Barium	>5000	>5000
Aluminum	1000	2000
Iron	1000	1000
Potassium	1000	1000
Strontium	800	800
Boron	250	40
Manganese	100	200
Titanium	60	60
Gallium	10	60
Silver	ND	10
Copper	ND	5
Molybdenum	ND	10

Observations of mineral precipitation/dissolution phenomena in natural systems can be generalized as follows: (1) minerals never precipitate from solutions that are undersaturated with respect to those minerals except in rare cases where biological activity facilitates it (Stumm and Morgan, 1981). An example is the precipitation of calcium carbonate by micro-organisms in sea water. If a solution passes through a reverse osmosis unit and remains undersaturated with respect to all mineral phases, it is extremely unlikely that any inorganic mineral scale will form; (2) minerals commonly do not precipitate from solutions that are slightly supersaturated. There is a nucleation barrier to mineral precipitation that commonly prevents minerals from precipitating (Morel and Hering, 1993). The degree of supersaturation that can be maintained without precipitating these phases is a complex function of time, temperature, the availability of favorable surface sites (such as suspended solids and types of surfaces available such as stainless steel, ceramics etc.), as well as the type of solid (silicate vs. carbonate etc.). It is not unlikely that some degree of supersaturation with respect to many mineral phases can be tolerated in a reverse osmosis unit without scale formation.

Our proposed pre-treatment process consists of three main steps (see dashed box in Figure 1): (1) addition of sodium carbonate (Na_2CO_3) while in contact with the atmosphere (aeration); (2) filtration to remove precipitates and suspended particles generated during Na_2CO_3 addition; and (3) addition of hydrochloric acid (HCl).

The addition of sodium carbonate increases the pH and increases the total carbonate content of the solution. Both factors decrease carbonate mineral solubilities and should cause the precipitation of these phases. Most of the carbonate added to the system will later be removed either as carbonate mineral precipitates or as CO_2 gas during the acidification step. This is an important advantage of using sodium carbonate versus other bases which may not speciate at low pHs to a gas. Filtration with a multimedia filter should be done only after addition of Na_2CO_3 in order to use available suspended solids as nucleation sites for mineral precipitation. Both the existing suspended particulates and fresh precipitates can then be removed by filtration prior to acidification. This step should remove most of the common solids that foul reverse osmosis membranes (i.e. sulfates, oxides, and carbonates).

Figure 2a shows the changes in concentrations of elements in solution as Na_2CO_3 is added to the mine water. These changes were calculated using the chemical reaction modeling program REACT (see Appendix 4). The concentrations decrease as carbonate minerals precipitate from solution. As more Na_2CO_3 is added, more minerals precipitate (amounts shown in Figure 2b; mineral compositions given on page 19) until about 0.05 moles of Na_2CO_3 have been added per liter of fluid after which there is little further effect. For economic reasons, we have chosen to limit the amount of added salt to only 0.006 moles of Na_2CO_3 per liter of fluid (see dashed line in Figure 2) in order to minimize the pre-treatment cost. The value of 0.006 was arrived at by an iterative method in which the goal was to add a minimum amount of Na_2CO_3 and still have the fluid remain undersaturated with respect to all solids after the reverse osmosis treatment. The chemical modeling simulator was run using arbitrarily chosen amounts of Na_2CO_3 until a minimum amount of the additive needed was determined. This process could automated with a feedback routine in the chemical modeling code algorithm.

Note that further benefit in terms of ending up with a fluid farther from mineral saturation is obtained by increasing the amount of added Na_2CO_3. However, as the amount of added Na_2CO_3 increases, so does the amount of acid (HCl) needed to neutralize the solution and the total cost of the pre-treatment process.

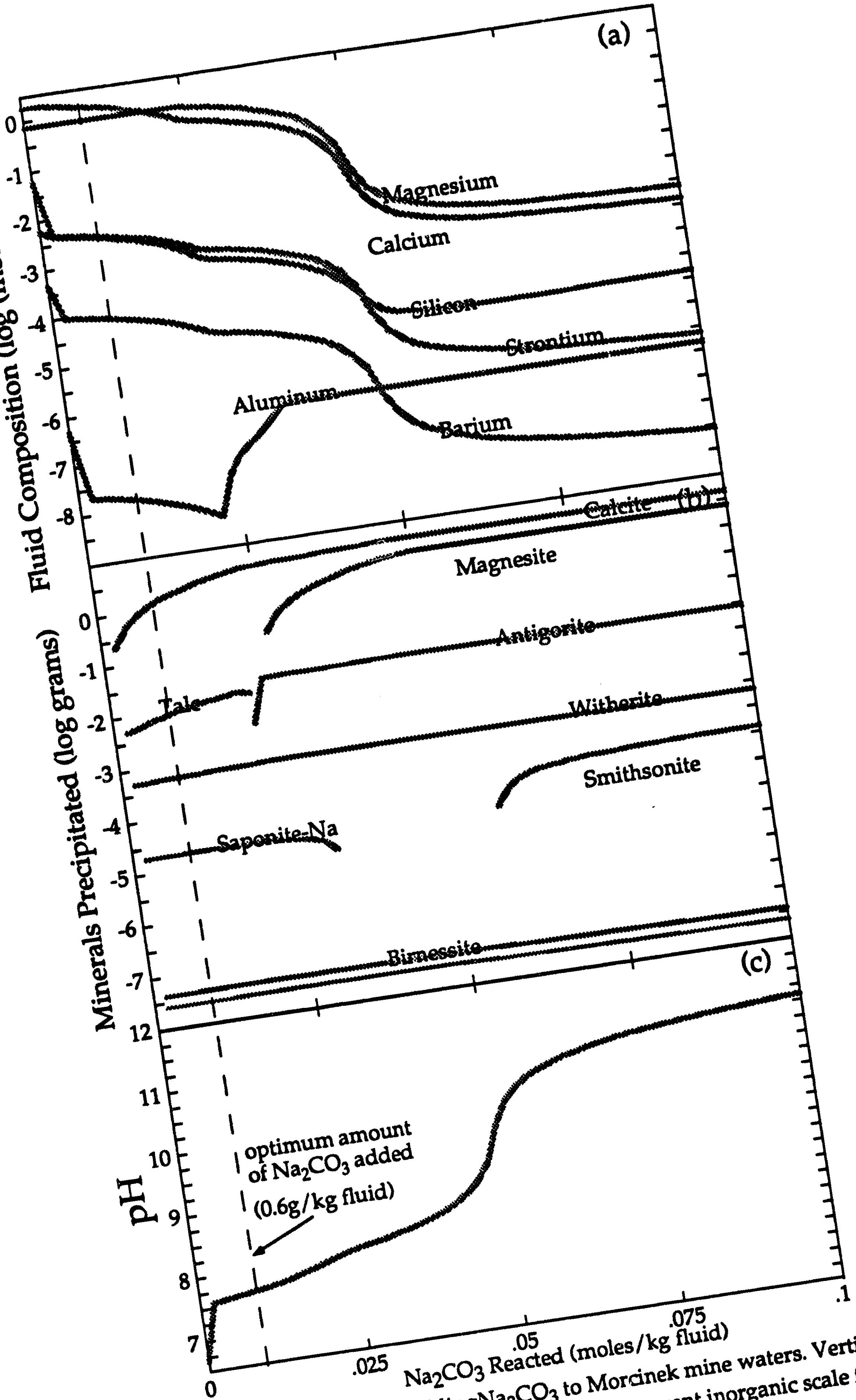


Figure 2. Chemical effects of adding Na_2CO_3 to Morcinek mine waters. Vertical dashed line indicates minimum required amount to prevent inorganic scale formation.

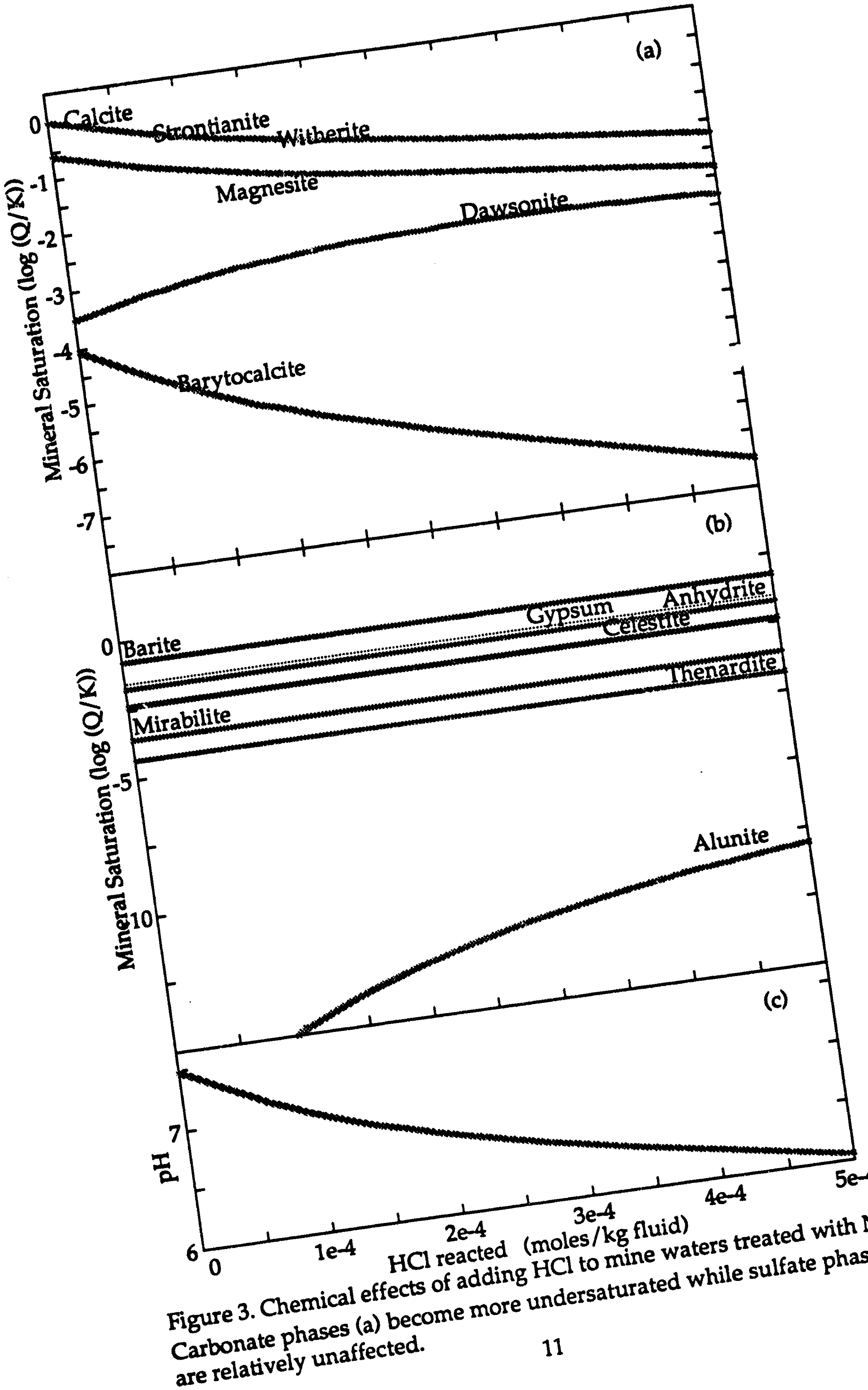


Figure 3. Chemical effects of adding HCl to mine waters treated with Na_2CO_3. Carbonate phases (a) become more undersaturated while sulfate phases (b) are relatively unaffected.

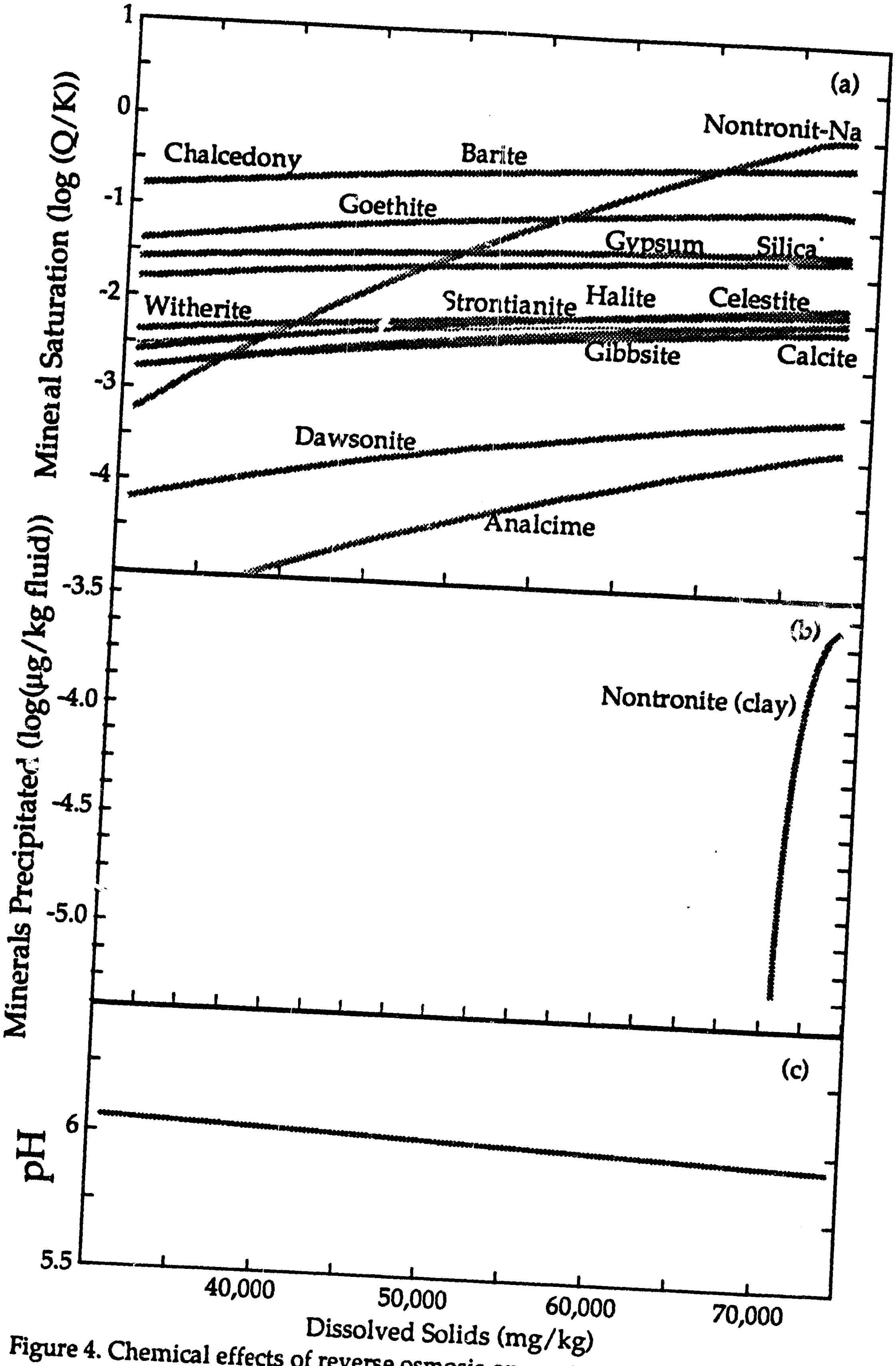


Figure 4. Chemical effects of reverse osmosis on pre-treated mine water. All phases remain undersaturated (min. sat.<0) during RO concentration until the TDS reaches 70,000 ppm, when a small amount of clay is predicted to precipitate.

Figure 2c shows the effect on pH of adding Na_2CO_3. There is initially little change in pH as most of the added Na_2CO_3 reacts with the fluid to precipitate carbonate minerals. It is this process which reduces the concentrations of the elements which might cause scaling in the RO membrane. Eventually the pH rises to values of greater than 10 with more Na_2CO_3 addition. In the actual addition of Na_2CO_3 to the mine fluid, there will be a small lag time of a few hours to as much as a day before the carbonate minerals precipitate out. This is not accounted for in the current simulation. The pH of the fluid can be used to monitor this lag time. The pH should rise to 10 or higher immediately upon addition of Na_2CO_3. As carbonates precipitate out, the pH will fall to the predicted value of around 7.8. When it has reached 7.8, no more minerals are expected to precipitate and there is no benefit to waiting any additional time before continuing with the fluid treatment process.

Table 3. Predicted fluid composition during pre-treatment and after reverse osmosis separation (in mg/kg). Column 3 shows predicted solution composition after equilibration with the atmosphere. Data are for adding 0.006 moles Na_2CO_3/liter fluid and .0005 moles HCl/liter fluid (see Table 4).

Element	Original Fluid	Aeration/ Oxidation	Na_2CO_3 addition	Acid Addition	After RO (brine)
Al	.03	.0003	1e-6	9e-6	2e-5
Ba	2	.28	.05	.05	.11
Ca	1170	1134	923	923	2205
Fe	0.3	1e-8	1e-8	1e-8	2e-8
Mg	460	446	445	445	1062
Mn	1.1	3e-5	5e-6	5e-6	1e-5
Na	10,300	9980	10,250	10,250	24,470
Si	6.5	3.5	1.9	1.9	4.6
Sr	42	30	2.3	2.3	5.6
Cl-	18,500	18,500	18,500	18,520	44,230
C	9.7	8.3	11.2	11.2	27
S	80	80	80	80	191
pH	7.5	6.6	7.5	6.1	5.9

$\log PCO_2$	-3.1	-2.3	-3.0	-1.9	-1.5
$\log PO_2$	-60	-2	-2	-2	-1.5
TDS	31,089	31,059	31,100	31,108	74,303

Aeration enhances the precipitation of iron and manganese hydroxides (along with silica in some cases) through the exposure of the fluid to atmospheric oxygen (see Table 3, column 3). Contact with air also will equilibrate the solutions with atmospheric carbon dioxide. Computer simulations predict that barium, and to a lesser extent strontium and calcium, will precipitate as carbonate minerals during aeration. These solids (as mineral grains or colloids) can be removed during a later filtration step before reverse osmosis treatment.

After removal of the suspended solids, the solution is then acidified to a pH of around 6 using hydrochloric acid. A pH of around six was chosen as optimum for reverse osmosis treatment both in terms of membrane performance and potential corrosion of the water treatment equipment (Brandt, Leitner and Leitner, 1993). Other pH adjustments may be designed for as needed. Figure 3 shows the predicted chemical effects during the addition of HCl to the mine fluid after addition of Na_2CO_3. Figure 3 shows the mineral saturation states (defined and explained in Appendix 3) of carbonate (3a) and sulfate (3b) minerals that have previously shown to scale reverse osmosis units. Minerals are saturated at a value of 0. Values greater than 0 correspond to minerals that are supersaturated and likely to cause scale formation; values less than 0 correspond to minerals that are undersaturated and will not cause scale formation. Our pre-treatment process is designed to insure that the saturation indices of all minerals are less than zero in the fluid coming out of the reverse osmosis unit. However, we have also minimized the amounts of added pre-treatment chemicals so that we add no more than is necessary to stay below the saturation limits. After acid addition, the resulting fluid is significantly undersaturated with respect to most solids (see Figure 3).

A simulation of the effect of concentrating the total dissolved solids (TDS) in the mine water during reverse osmosis is shown in Figure 4. As can be seen (Figure 4a) no minerals become saturated in the mine water until the TDS reaches about 70,000 ppm, when a small amount of clay phase (Figure 4b) is predicted to precipitate. Therefore it is not anticipated that water removal during reverse osmosis will cause any inorganic scaling of the RO membrane. The pH increases slightly during RO treatment (Figure 4c).

Simply adding acid to the mine waters without the step of adding Na_2CO_3 does not prevent mineral precipitation. The solubilities of sulfate minerals such as barite ($BaSO_4$), gypsum ($CaSO_4.H_2O$) and celestite ($SrSO_4$) are relatively insensitive to pH. Modeling calculations which simulate the addition of HCl to the mine fluid without the intermediate sodium carbonate step show that the fluids will continue to precipitate barium and strontium minerals during the reverse osmosis treatment. These metals (or the sulfate) must be removed from the fluids before they enter into the reverse osmosis unit in order to prevent scale formation.

HCl is preferred over common acids such as sulfuric because the chloride anion forms few stable solids. Sulfate forms stable solids with numerous cations, such as Ba, Sr, Ca. Adding sulfuric acid pushes the fluid closer to saturation with respect to these phases than does HCl. However, cost considerations may dictate whether hydrochloric or sulfuric acid (or some mixture) is used. Nitric acid is also not preferred because of it's potential to oxidize the RO membrance and the factc that nitrate availability may encourage microbial growth.

Ultrafiltration to remove particles as small as 0.1 microns should be used to remove any remaining suspended load before passage into the reverse osmosis unit. Economic factors will determine whether ultrafiltration is performed before or after HCl addition. Ultrafiltration before HCl addition will minimize the amount of HCl that needs to be added. This is because the suspended load of very fine particles will tend to dissolve in the presence of the acid. More acid will therefore be necessary to get to the desired pH. On the other hand, ultrafiltration after HCl addition will extend the lifetime of the filters because of the reduced numbers of fine particles, some of which have reacted with the previously added HCl and dissolved. The tradeoff is between the cost of supplying and cleaning the filters, and the cost of HCl.

After pre-treatment, the brine that is delivered to the reverse osmosis unit will have a total dissolved salt content (TDS) of about 30,700 mg/kg. The reverse osmosis unit will separate the brine stream in to a potable water stream having a TDS of 500 ppm and a stream of concentrated brine. The optimum economic concentration of the brine by the reverse osmosis unit will depend on a number of technical and economic factors that have not yet been fully determined. For this study, however, we have assumed that the concentrated brine stream leaving the reverse osmosis unit will have a concentration of about 70,000 mg/kg. An additional calculation was made that shows no negative effects other than the precipitation of a small amount of clay mineral if the TDS load of the output brine increases to over 100,000 ppm.

The masses of commercially available chemical additives to be used in the pre-treatment process are listed in Table 4.

DISCUSSION OF PRE-TREATMENT

Oxidation and carbonation of waters through reaction and equilibration with the atmosphere commonly does not take place to completion (Stumm and Morgan, 1981). Analyses of most surface waters shows that they are partially oxidized and approaching equilibration with atmospheric carbon dioxide. Solutions tend to remain at metastable high carbon dioxide levels (don't de-gas completely), and oxidation of reduced metals to more oxidized forms is usually slow at ambient temperatures. We have calculated the effect of equilibration with the atmosphere on the mine waters in order to determine the solubilities of elements. This information tells us whether or not the fluid/atmospheric interactions should be enhanced or avoided before the fluids pass into the reverse osmosis unit. Table 3 (column 3) shows the results. The concentrations of iron, barium, aluminum, and manganese are all greatly reduced. Atmospheric contact with these solutions should therefore be maximized.

The calculation for the effect of adding Na_2CO_3 reported here, however, does not assume atmospheric equilibration. Additional benefit, beyond that in these calculations, in reducing the amounts of dissolved Fe, Al, Ba, and Mn may be expected due to reaction of the mine fluid with atmospheric gases (O_2 and CO_2). Interactions of the mine water with the atmosphere should therefore be maximized during pre-treatment (e.g. spraying or bubbling).

Table 4. Masses of additives needed in pre-treatment process.

Reagents Added in Pre-treatment Process						
Stage	Moles per kg fluid	Grams per kg fluid	Kg per m^3 fluid	Lbs. per m^3 fluid	Lbs. Product per m^3 fluid	Product
Add Na_2CO_3	0.006	.636	.655	1.44	1.69	Monohydrate
Add HCl	0.0005	0.020	0.021	0.045	0.123	12 Molal HCl

Soln. density	1.03	gm/cm^3
Wt/m^3 fluid	1030	kg/m^3
KG->LBS	2.205	lbs/kg

Commercially Available Products			
Name	Mol. Wt.	Wt % HCl or Na_2CO_3	Description
Na_2CO_3	105.99	100.0	Anhydrous
$Na_2CO_3.H_2O$	124.00	85.5	Monohydrate‡
$Na_2CO_3.NaHCO_3.2H_2O$	226.03	–	Sesquihydrate
$Na_2CO_3.7H_2O$	232.10	45.7	Heptahydrate
$Na_2CO_3.10H_2O$	286.14	37.0	Decahydrate
Conc. HCl	36.46	37	12 Molar acid
HCl(gas)	36.46	100	Pure Gas
‡the mineral Thermonatrite			

Besides inorganic scaling, some types of biological activity are adverse to membrane performance. Biofilms may form on the membrane and interfere with passage of water through the pores (Flemming, 1993). Bacteria themselves also can cause clogging. Our proposed treatment for the inorganic scalants has a favorable effect on potential biological problems as well. Changes in pH such as will occur during the addition of sodium carbonate and HCl to the mine water will kill many of the natural bacteria present because most individual species of bacteria can only live in a restricted pH range (Gaudy and Gaudy, 1980; Laskin and Lechevalier, 1974). Additional benefit may be achieved by increasing the amount of HCl added so that the final brine has a pH of about 2, in order to kill more micro-organisms (Stolp, 1988). Model calculations indicate that if the amount of HCl added is increased from 0.005 to 0.015 moles/kg fluid (.13 to .39 pounds of product) the final pH will be 1.9. it may also be important to keep light away from the mine fluid to prevent growth of algae and other photosynthetic organisms.

Note that in Figure 1, treatment with Na_2CO_3 is shown in pond 1 and treatment with HCl is shown in pond 2. Alternative procedures may be more effective and need to be considered. For example, it may be better to aerate and add Na_2CO_3 in pond 1, and use pond 2 as a settling pond (see Figure 5). Aeration may keep the suspended load high due to agitation, both by the aeration process (if used) and by wave action in the exposed pond. The suspended load should be as low as possible to prevent membrane clogging and fouling. It may be worthwhile to cover pond 2 to prevent stirring due to wave action and allow settling of suspended particles to take place there. The HCl can be added in a small batch reactor prior to entering the reverse osmosis unit. Economic factors may determine the optimum use of the 2 ponds.

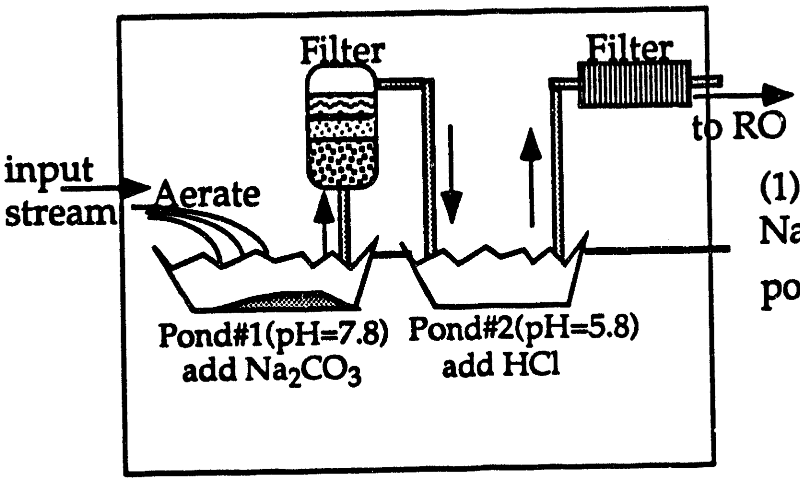
POST-REVERSE OSMOSIS FLUID CHEMISTRY

The brine from the reverse osmosis unit is delivered to the submerged combustion evaporator (Figure. 1). In submerged combustion evaporation, combustion gases obtained in the combustion of methane with air (approximately 75 per cent excess air) are vented through the brine in the evaporator. The hot gases cause water to be evaporated from the brine. A recirculation pump recirculates the brine in the evaporator and a discharge control valve in the recirculation line permits the discharge of concentrated brine from the evaporator at a controlled rate. By balancing the feed rate of the brine delivered to the evaporator, with the brine discharge rate and the rate of water evaporation, a steady state operating condition can be reached. At steady state operation, the evaporator typically operates with a brine having a concentration of 300,000 mg/kg dissolved salt in contact with a suspension of solid salt particles.

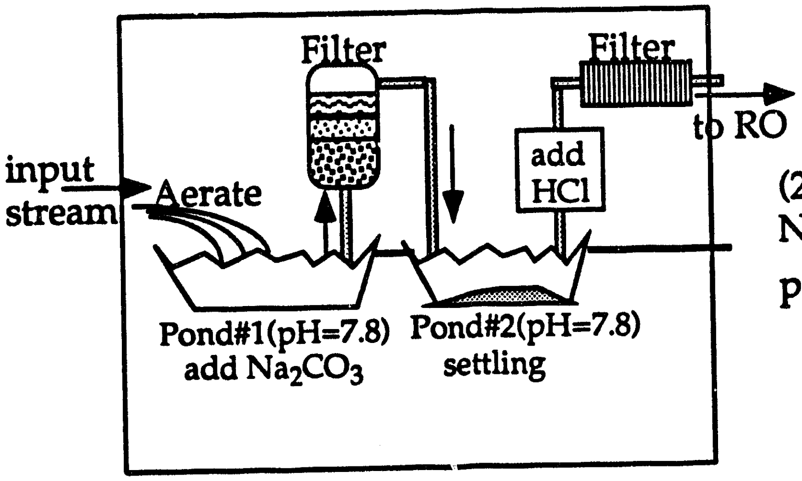
The gases that are vented into the atmosphere consist substantially of combustion products resulting from the combustion of methane and air, and water vapor evaporated from the brine. In addition, the potential exists for volatile components and small brine droplets to be vented into the atmosphere. Brine droplets are removed from the exhaust stack by means of scrubbers.

CONCLUSIONS

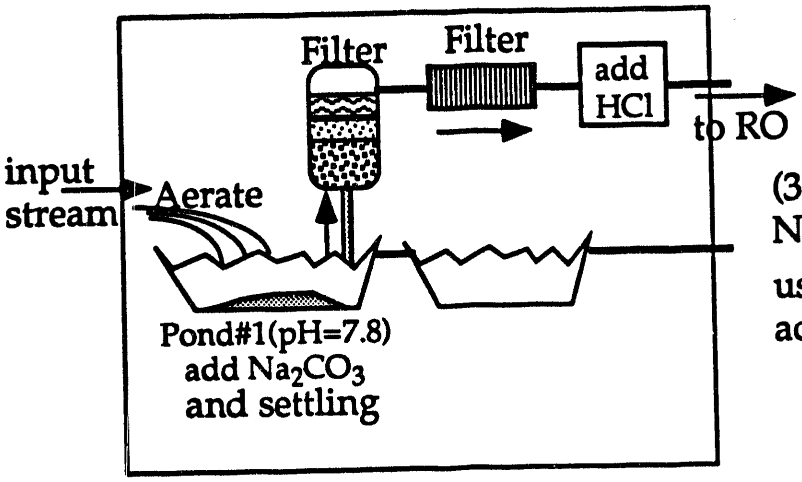
For a brine feedstream of $100m^3$, 170 lbs. of $Na_2CO_3 \cdot H_2O$ and 13 lbs. of concentrated hydrochloric acid would need to be added during the reverse osmosis pre-treatment process. The potable water from the reverse osmosis unit would have a salt concentration of 500 ppm and the salts in the potable water would substantially consist of Na^+ and Cl^- which would make the water potable. The brine delivered to the submerged combustion evaporator would have a salt concentration of about 70,000 mg/kg.



(1) Use pond 1 for adding Na_2CO_3 and settling, pond 2 for acidification.



(2) Use pond 1 for adding Na_2CO_3 and aeration, pond 2 for settling.



(3) Use pond 1 for adding Na_2CO_3 and settling, don't use pond 2, filter before acid addition.

Figure 5. Some pre-treatment filtering and pond use options.

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Appendix 1. Mineral names and formulas.

Alunite	$KAl_3(SO_4)_2(OH)_6$	
Analcime	$NaAlSi_2O_6.H_2O$	(zeolite)
Anhydrite	$CaSO_4$	
Antigorite	$(Mg,Fe)_3Si_2O_5(OH)4$	(clay)
Barite	$BaCO_3$	
Barytocalcite	$BaCa(CO3)_2$	
Bassanite	$2CaSO_4.H_2O$	
Birnessite	$Na_4Mn_{14}O_{27.7}7H_2O$	
Calcite	$CaCO_3$	
Celestite	$SrSO_4$	
Chalcedony	SiO_2	
Dawsonite	$NaAl(CO_3)(OH)_2$	
Gibbsite	$Al(OH)_3$	
Gypsum	$CaSO_4.H_2O$	
Halite	NaCl	
Magnesite	$MgCO_3$	
Mirabilite	$Na_2SO_4.10H_2O$	
Nontronite	$NaFe_6AlSi_{10}O_{30}(OH)_6$	(clay)
Saponite-Na	$NaMg_9AlSi_{11}O_{30}(OH)_6$	(clay)
Smithsonite	$ZnCO_3$	
Strontianite	$SrCO_3$	
Talc	$Mg_3Si_4O10(OH)_2$	(clay)
Thenardite	Na_2SO_4	
Witherite	$BaCO_3$	

Appendix 2. Fluid sampling procedure.

These procedures are recommended for sampling well waters under normal field conditions and were used to collect the Polish mine water samples. Although it is impossible to obtain an exact representative sample, these procedures should help to minimize most common problems and allow useful sample to be obtained.

1. Flush the system by letting the water run until a volume of at least two times the volume of the sample plumbing system has been released.

2. Fill up a clean container of fluid for pH and temperature measurements. Take these measurements as soon as possible. Equilibration with atmospheric gases (oxygen and carbon dioxide) cause changes in fluid chemistry. These effects can be minimized by taking the measurements as soon as possible (within a few minutes).

3. Draw 10 ml of fluid into a plastic syringe, attach a 0.45 micron filter disk to the end of the syringe and inject the fluid into a pre-acidified cation sample tube. This step filters the fluid and acidifies it to prevent any precipitation of dissolved species.

4. Draw 10 ml of fluid into a plastic syringe, attach a 0.45 micron filter disk to the end of the syringe, and inject the fluid into an anion sample tube. This sample was used for anion (chloride, fluoride, nitrate etc.) analysis using liquid chromatography.

5. Draw 10 ml of fluid into a plastic syringe, attach a 0.45 micron filter disk to the end of the syringe, and inject the fluid into the carbon dioxide sample tube. This tube contains a small amount of KOH solution which keeps all dissolved carbon dioxide in solution. This sample was used for carbon dioxide analysis.

6. Fill a 250ml high-density polyethylene (HDPE) bottle completely with fluid as a backup sample.

7. Fill a glass vial with Teflon septum top with fluid. This sample will be used for analysis of organic compounds.

8. Label all containers.

Appendix 3. Definition of mineral saturation indices.

The mineral saturation index (log(Q/K) referred to in the text and plotted in Figures 3 and 4 is a measure of the saturation sate of a solid with respect to a solution. When a solid is undersaturated, it tends to dissolve until saturation is achieved. When a solid is supersaturated, it tends to precipitate out of solution until it is saturated. The rates of these reactions are functions of temperature, the extent to which the solid is under or super-saturated, and the type of solid.

The ratio Q/K refers to the concentration product of species in solution (Q) divided by the concentration product at equilibrium (K). K is also referred to as the solubility product. For example for calcite, the solubility reaction can be written as:

$$CaCO_3(s) = Ca^{++} + CO_3^{--}$$

The solubility product is $[Ca^{++}][CO_3^{-}]$ where the brackets refer to concentrations (or rigorously, thermodynamic activities) of the dissolved species at equlilibrium. At a given temperature and pressure, a solution in equilibrium with calcite has a fixed value for the concentration product, called the solubility product (K). For a solution not at equilibrium with calcite, the concentration product (Q) will not be equal to the solubility product. If calcite is undersaturated, $Q<K$ and $\log (Q/K)<0$; if calcite is supersaturated, $Q>K$ and $\log (Q/K)>0$. The solubility product can therefore be used as a predictor of the potential for membrane scaling. The purpose of these simulations is to insure that the fluids passing through the RO membrane always have saturation indices of less than zero for all mineral phases.

Figures 3 and 4 show desired conditions where the mineral phases are undersaturated with respect to the mine water, even during concentration of the dissolved species during reverse osmosis. One goal of the pre-treatment is to produce a fluid that is always undersaturated with respect to all mineral phases. However, only the minimum amount of pre-treatment chemicals should be added in order to minimize costs. Therefore the overall goal is to generate a fluid that approaches but does not exceed saturation at the end of the reverse osmosis process. On Figure 4 this is shown where the clay mineral Nontronite reaches saturation when the TDS of the mine water during treatment reaches 70,000 ppm. The simulation predicts that a small amount of nontronite will precipitate out in the RO unit during concentration of the input fluid at TDS levels greater than 70,000 ppm.

Appendix 4. Chemical reaction modeling code REACT.

The computer modeling code REACT (Bethke, 1992) and the LLNL thermodynamic database DATA0.COM.R46 (reformatted to be read by REACT) were used for all the simulations. The database contains thermodynamic values for over 1000 solids, gases, and aqueous species common in natural fluids, rocks, and soils. The database coves the temperature range of 0-300°C. Plots included in this report were generated using the REACT graphics post-processor GTPLOT.

REACT is a reaction path chemical modeling code that iteratively solves the set of mass action and mass balance equations that describe chemical equilibria. The simulations reported here consisted of defining a starting fluids composition, and then modifying that composition by reacting the fluid with another fluid or solid. The code calculates the consequences of that reaction, including provisions for mineral precipitation and dissolution, changes in ionic strength and activity coefficients, gas solubilties, and re-distributes the aqueous species defined by these new conditions. The simulation of reverse osmosis was done by simply removing water from the pre-treated fluid.

REACT also has provisions for kinetic control of mineral dissolution/precipitation. This option was not used in the present modeling but may be used in the future. In the present simulations, minerals were assumed to precipitate immediately upon reaching saturation, and were forced to remain at saturation from that point on. There were no provisions for any nucleation barrier to precipitation, or precipitation rates being dependent upon the degree of supersaturation. The effects of these simplifying assumptions are not believed to be significant because carbonate mineral precipitation/dissolution rates are relatively rapid on the timescale of our pre-treatment process, as discussed briefly above and in (Herman and Lorah, 1988).

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