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Produced Water Pretreatment for Water Recovery and Salt Production
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Produced Water Pretreatment for Water Recovery and Salt Production

James M. Silva, Hope Matis, William L. Kostedt IV, and Vicki Watkins

Abstract:

Horizontal drilling and slickwater hydrofracturing have enabled shale gas to become a significant contributor to the United States' energy supply. Hydrofracturing typically requires 2MM – 6.5MM gallons of water per shale gas well. About 15-25% of this water returns to the surface as "flowback" within 30 days after hydrofracturing. "Produced water" continues to flow at a much reduced rate, e.g. 2-10 bbl/day, for the life of the well. In addition to high salinity and hardness levels (Mg, Ca, Sr, Ba), much Marcellus produced water also contains significant levels of naturally occurring radioactive materials (NORM), particularly radium. The near absence of disposal wells in Pennsylvania initially forced much of the produced water to be trucked into Ohio for disposal by deep-well injection (UIC). Currently up to 95% of the flowback and produced water is reused in subsequent hydrofracturing operations. However, eventually the supply of flowback and produced water is expected to exceed the reuse capacity. At this point, a growing volume of high-TDS produced water must either be deep-well injected, or water and salt recovery is required. The objective of this study is to identify cost-effective softening technologies, primarily for barium and radium removal, that enable thermal recovery of distilled water and a salable salt product from produced water.

Current technology utilizes evaporation to recover about 56% of the produced water as distilled water and a salt concentrate, which is disposed of by UIC (design case). To achieve 80-95% water recovery, it is necessary to generate a solid salt (NaCl) product. For use as road salt, the salt product TCLP extract must contain no more than 100 mg/L barium. It is also assumed that the salt product must also meet ^{226}Ra specifications for disposal of solids as nonhazardous solid waste, which is 25 pCi/gm in Pennsylvania. Based on a pilot study by GE Water and Process Technologies (GEWPT) of Marcellus produced water evaporation and salt crystallization, we defined a map of pretreatment needs as a function of the produced water barium and radium concentrations. We concluded that produced waters containing less than a specific barium concentration ($[Ba]_{max}$, about 1,000-2,000 mg Ba/L) and essentially arbitrary radium activities do not require barium removal prior to NaCl crystallization ("Type I" produced water). Produced water with a barium concentration greater than $[Ba]_{max}$ and very low radium activity (<200-1,000 pCi ^{226}Ra/L; upper limit depends on the produced water barium concentration) may be economically treated for barium removal by sulfate precipitation ("Type II" produced water) prior to NaCl crystallization. Produced water with a barium concentration greater than $[Ba]_{max}$ and higher radium activity (>200-1,000 pCi ^{226}Ra/L; lower limit depends on the produced water barium concentration) requires barium removal by a method other than direct sulfate precipitation prior to NaCl crystallization ("Type III" produced water). We focused on defining economical pretreatment processes for Type III produced water.

Selective removal of radium from Type III produced water in order to enable barium removal by sulfate precipitation is not practical.   We found that the radium capacity of DOWEX™ RSC, a commercially available ion exchange resin for radium removal from aqueous streams, is too low to be economical.

We defined two pretreatment processes to remove both barium and radium from Type III produced water. Each process generates a barium and radium concentrate waste stream that may be disposed of by UIC. The first process utilizes a modified lime-soda softening process to completely soften produced water. Magnesium, calcium, and strontium are first selectively precipitated to yield a solid sludge that may be disposed of as nonhazardous waste in a RCRA-D facility. This is followed by precipitation of barium and radium as carbonates. The carbonates from the second precipitation step are redissolved with HCl to yield a liquid concentrate that can be disposed of by UIC. For the design case, about 0.05 bbl of concentrate for UIC disposal and about 25 lb. RCRA-D solid waste are generated per bbl raw produced water. For this case, the materials and disposal cost is estimated to be $3.5/bbl produced water. Further development work is needed to maximize the selectivity of the first precipitation step for calcium and strontium over barium and radium and to reduce the materials cost.

The second process utilizes high surface area, HCl-regenerable MnO_2 as an adsorbent for barium and radium. The estimated materials and disposal costs for this process are in the range of $1.7-$2.3 per bbl produced water for the design case produced water (10, 5 cycles of adsorbent life, respectively). Because this process utilizes micron or submicron MnO_2 particles, further work is required to define cost-effective particle-water separation processes for both produced water treatment and MnO_2 regeneration. In addition, MnO_2 regeneration requires dilute HCl (ca. 0.1N), but the regeneration product for UIC disposal is a $BaCl_2$-$RaCl_2$ concentrate. MnO_2 regeneration with a solution of dilute HCl and concentrated $BaCl_2$-$RaCl_2$ needs to be demonstrated in the laboratory.

Both processes have undergone preliminary laboratory scoping studies with field produced waters. It is recommended that the modified lime-soda process be further developed in the laboratory in preparation for pilot-scale testing. It is also recommended that the further laboratory development of the MnO2 adsorption process be conducted. This process has potential for lower treatment and disposal costs than the modified lime-soda process. It is also recommended that additional laboratory and pilot evaporation and crystallization studies be conducted with field produced waters to better define [Ba]max.

Signature and Date Stamp

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January 26, 2012

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I. Introduction

Horizontal drilling and slickwater hydrofracturing have enabled shale gas to become a significant contributor to the United States' energy supply. Developed largely in the Barnett shale, these technologies have more recently been applied to the Marcellus shale, which has the potential to become the second largest natural gas field in the world[1]. Hydrofracturing a shale gas well typically requires 2MM – 6.5MM gallons of water. About 15-25% of this water returns to the surface as "flowback" within 30 days after hydrofracturing. "Produced water" continues to flow at a much reduced rate, e.g., 2-10 bbl/day, for the life of the well. It is estimated that in Pennsylvania, in 2011, about 25 MM bbl of flowback and produced water will be generated[2]. A potential limitation to developing the Marcellus is the disposal cost of hydrofracturing flowback and produced water, which are collectively referred to as "frac" water in this report. In addition to high salinity and hardness levels (Mg, Ca, Sr, Ba), much Marcellus produced water also contains significant levels of naturally occurring radioactive materials (NORM), particularly radium. The near absence of disposal wells in Pennsylvania initially forced much of the produced water to be trucked into Ohio for disposal by deep-well injection (UIC[3]). The cost of trucking from eastern Pennsylvania to Ohio and disposal by UIC is in the range of \$10-12/bbl[4].

Since 2009, there has been a significant increase in frac water reuse for subsequent hydrofracturing jobs. Current estimates of Pennsylvania Marcellus frac water reuse (after various forms of pretreatment) range from about two-thirds[5] to about 95%[2]. Because *flowback* water has much lower TDS[6] than *produced* water, flowback water is more likely to be reused in subsequent hydrofracturing operations than produced water. Recovered frac water is often reused with significant dilution by fresh water. Even assuming 95% reuse, there is still an average of approximately 0.15-0.3 MM gallons per day of produced water in the Pennsylvania Marcellus shale gas play that must be disposed of by UIC[7]. As the number of shale gas wells within a given geographic region (e.g. a county) grows, the supply of produced water with high TDS levels (viz. TDS levels at or above about 125,000 ppm) also grows. This increase is due to the lengthy production lifetime of the shale gas wells, each of which continually yields produced water. Reuse also increases the TDS level of the produced water. Based on an analysis by Hayes[8], for a given geographic area, sometime after the rate of hydrofracturing and refrac operations peaks, the supply of produced water is expected to exceed the reuse capacity. At this point, a growing volume of high-TDS produced water must either be deep-well injected, or water and salt recovery is required.

There has been much recent regulatory activity with respect to frac water disposal, particularly in Pennsylvania. For example, since May 19, 2011, in Pennsylvania, shale gas drillers have been directed by PADEP to cease delivering wastewater to the 15 wastewater treatment plants that had been accepting it and had been granted "grandfather" status with respect to PADEP's 2010 Total Dissolved Solids regulations. These wastewater treatment plants include Publicly Owned Treatment Works (POTW) and Centralized Wastewater Treatment (CWT) facilities[9].

The purpose of this study is to identify pretreatment technologies that enable economic recovery of distilled water and a salable salt product from high-TDS Marcellus shale gas produced water. The high TDS levels in the produced water require thermal processes (evaporation and crystallization) for economic water and salt recovery. Pretreatment technologies include both softening (primarily barium removal) and NORM removal. Softened produced water enables a higher recovery of both distilled water and salt product, compared with non-softened water. Consistent with these higher recoveries, the crystallizer purge stream, which must be disposed of by UIC, is smaller with softened water than with non-softened water.

In produced water, soluble NORM species comprise ^{226}Ra and ^{228}Ra, which are daughter products of naturally occurring ^{238}U and ^{232}Th, respectively. ^{226}Ra is of principal interest because of its long half-life (1600 years), its water solubility as a divalent cation, and its status as a known carcinogen[10,11]. ^{226}Ra is an alpha emitter (4.781 MeV) and a gamma emitter (186.2 keV). The ^{228}Ra activity[12] was typically less than 10% of the ^{226}Ra activity for the water samples analyzed from the Marcellus Shale formation[13]. For removal processes, it is expected that ^{226}Ra and ^{228}Ra will behave similarly. Therefore, with respect to NORM, this study is focused on ^{226}Ra.

We defined a "design case" produced water composition based on data from the literature as well as seven produced water samples that we obtained (six from the Pennsylvania Marcellus and one from the Barnett). For the design case, current water recovery technology comprises evaporation to recover about 56% of the produced water as distilled water. This process also yields a salt concentrate, which is disposed of by UIC.

To achieve 80-95% water recovery, it is necessary to generate a solid salt product. For use as road salt, the solid salt (NaCl) product must pass TCLP[14], which includes the requirement that the TCLP extract of the salt product contain less than 100 mg barium/L. Although there is currently no radium specification for road salt in either New York or Pennsylvania[15], it is assumed that road salt must meet ^{226}Ra specifications for disposal of solids as nonhazardous solid waste, which is 25 pCi/gm in Pennsylvania.

Based on a GEWPT pilot study of Marcellus produced water evaporation and salt crystallization, we defined three types of produced water based on their barium and radium concentrations. Each type of produced water requires a different pretreatment process to enable recovery of a salt product. "Type I" produced waters contain less than a specific barium concentration, $[Ba]_{max}$, (~1,000-2,000 mg Ba/L) and are not restricted with respect to ^{226}Ra activity. Type I produced waters require neither barium nor radium removal prior to NaCl crystallization.

“Type II” produced waters contain a higher barium concentration than $[Ba]_{max}$ and very low radium activities (<200-1,000 pCi ^{226}Ra/L; upper limit depends on the produced water barium concentration). Type II produced waters may be economically treated for barium and radium removal by conventional sulfate precipitation prior to NaCl crystallization.

“Type III” produced waters contain a higher barium concentration than $[Ba]_{max}$ and higher radium activities (>200-1,000 pCi ^{226}Ra/L; lower limit depends on the produced water barium concentration). Type III produced waters require barium removal using a method *other than direct sulfate precipitation* prior to NaCl crystallization. In this project, we focused on defining economical barium and radium removal pretreatment processes for Type III produced waters.

We explored several classes of adsorbents to selectively remove radium from produced water, which would enable barium to be subsequently removed by sulfate precipitation. DOWEX™ RSC (radium-specific complexer) has been utilized to remove radium in municipal water systems[16]. However, we found that the ^{226}Ra capacity for RSC (and all other adsorbents screened) was too low to economically remove radium from produced water.

We considered ion exchange and nanofiltration as potential methods of softening Type III produced water. Based on the design case produced water composition, we found that neither process was economically attractive. For ion exchange, the cost of regeneration chemicals and waste disposal was over $6/bbl produced water. In addition, the ion exchange regeneration waste volume would be comparable to the volume of produced water being treated. For softening by nanofiltration, simulations showed that the water recovery fraction would be too low to be economical.

We identified two processes to remove barium and radium from Type III produced water[17]. The byproduct from each process is a concentrated solution of barium and radium that may be disposed of by UIC. In the first process, the produced water is completely softened by a modified lime-soda process. After magnesium is precipitated as a hydroxide, calcium and strontium are precipitated as carbonates and disposed of as nonhazardous waste in a RCRA-D[18] landfill. A second step precipitates barium and radium as carbonates. After these carbonate salt solids are removed from the produced water, they are redissolved by addition of HCl to form an aqueous solution of $BaCl_2$ and $RaCl_2$, which is disposed of by UIC. For the design case produced water, the cost of materials and disposal for this process is $3.5/bbl produced water.

In the second process, barium and radium are removed from produced water by adsorption onto a MnO_2 adsorbent. This adsorbent is regenerated by dilute HCl treatment, which yields a $BaCl_2$-$RaCl_2$ concentrate for disposal by UIC. For the design case produced water, the cost of chemicals and disposal for this process is $1.7-$2.3/bbl produced water (based on 10 and 5 adsorption-regeneration cycles, respectively). This report shows laboratory experimental results and costs for both processes.

II. Produced Water Composition

A. Literature Data

Figure 1 shows volume and TDS flowback profiles for a characteristic hydrofractured well in the Marcellus. This figure was constructed from flow and composition data presented by Vidic[19]. The flowrate is relatively high through Day 6 and then drops to a relatively constant rate through Day 22. The instantaneous TDS increases essentially monotonically throughout the first 17 days and then plateaus at about 150,000 mg/L. About 27% of the water used to hydrofracture the well returned within 22 days.

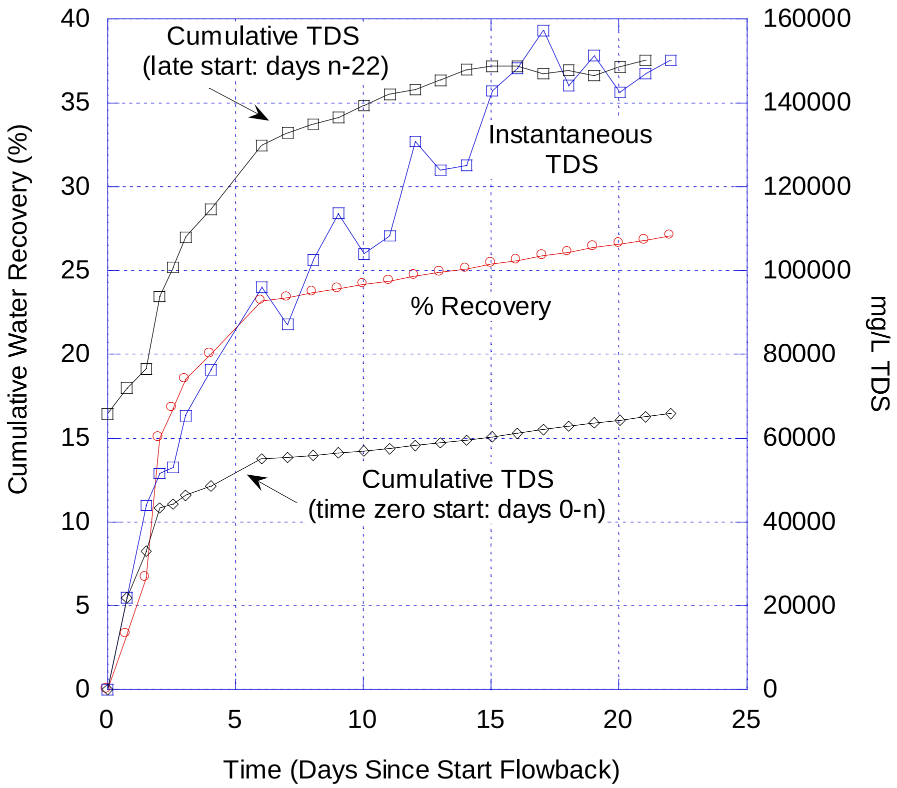

Figure 1. Marcellus Shale Flowback and Produced Water Profiles

Two cumulative TDS levels are also plotted. Each point on the line labeled "Cumulative TDS (time zero start: Days 0-n)" represents the volume average TDS of the flowback and produced water between the beginning of flowback (Day 0) and Day "n". The value of this cumulative TDS measurement for Day 15 is about 60,000 mg/L. Currently, in the Marcellus, much of the early flowback water is reused with minimal treatment (e.g. removal of suspended solids and bacteria, with optional softening). In this example, the cumulative TDS for the first five days is about 50,000 mg/L and represents about 80% of the water returned during the first 22 days. This water could be minimally treated and reused in subsequent hydrofracturing jobs.

Each point on the line labeled "Cumulative TDS (late start: Days n-22" represents the volume average TDS for the time interval from Day "n" through Day 22. The value of this cumulative

TDS measurement for Day 6 is about 130,000 mg/L. This value represents the volume average TDS for flowback and produced water collected from Day 6 through Day 22. Flowback and produced water from this interval may be pretreated and thermally recovered as distilled water and salt.

Keister[20] reported frac water compositions, giving values for low-, medium-, and high-TDS frac water, as well as a "typical" frac water. Table 1 shows the values reported by Keister.

A private report of Marcellus frac water composition was prepared for the Marcellus Shale Coalition[21]. This report surveyed frac waters from 19 locations during both the early flowback period (1-5 days) and later periods (14, 90 days). The range and median values of TDS and specific ion concentrations reported are consistent with values shown in Table 1 and in the samples that we obtained (discussed in Section II-B below).

Table 1. Marcellus Frac Water Compositions

(all concentrations in mg/L)

Component	Low-TDS	Medium-TDS	High-TDS	"Typical"
TDS	69,640	175,300	248,000	195,000
Mg	438	938	1,630	1,300
Ca	5,140	14,100	31,300	18,000
Sr	1,390	6,830	2,000	4,000
Ba	2,300	3,310	4,300	6,500
Fe	11.2	52.5	134	60
Mn	1.9	5.17	7	5.0

B. Produced Water Samples

We obtained Marcellus shale gas produced water from horizontal wells in four Pennsylvania counties. Samples were obtained from either portable frac tanks adjacent to a recently hydrofractured well or from a permanent tank at a well site. In addition, one sample was taken from a salt water disposal facility in the Barnett Shale (Texas).

Table 2 shows the measured composition for these samples. All ionic species were measured by inductively coupled plasma (ICP). Only one sample (Well-4) had a measurable level of sulfates; the same sample had a very low barium level. The appearance of the frac water samples when received ranged from clear to orange-brown.

The level of ^{226}Ra in each sample was measured using gamma spectrometry. Several of the ^{226}Ra gamma spectrometry measurements were conducted both at GEGR and at the New York State Department of Health, with excellent agreement between the two sites. The GEGR results are reported in Table 2.

Based on the measured composition of the Marcellus produced water samples shown in Table 2, we identified a design case produced water composition ("Design Case"). For the design case, each species concentration approximates the median of the measured concentrations.

Table 2. Produced Water Compositions from Pennsylvania Marcellus Shale Gas Wells.
(all quantities mg/L except where noted)

	Well-1	Well-2	Well-3	Well-4	Well-5	Well-6	Well-7[a]	Design Case
County	Bradford	Bradford	Bradford	Butler	Tioga	Washington		
pH[b]	7.3	6.3	5.4	5.8	5.9	6.2	6.6	7.0
TDS	98,294	155,705	199,242	68,439	149,188	122,562	124,421	132,460
Na^+	26,500	38,200	51,800	19,200	39,000	32,300	33,900	35,000
Mg^{++}	460	840	1290	570	1,000	800	1,170	800
Ca^{++}	5,560	10,280	13,120	5,360	13,000	8,700	10,880	9,500
Sr^{++}	2,030	3,670	4,580	1,290	2,600	2,340	1,750	2,500
Ba^{++}	6,580	13,200	11,600	32	3,500	5,800	147	6,200
Fe^{++}	26	74	123	55	32	75	47	50
Mn^{++}	1.5	2.5	3.4	1.7	2.7	4.3	1.2	3
Cl^-[e]	57,120	89,429	116,713	41,845	90,014	72,525	76,493	78,407
$SO_4^=$	<10	<10	<10	57	<5	<50	<100	0
SiO_2	16.7	11	13	29	39	18	33	0
Hardness as Ca^{++}	9,167	17,196	20,727	6,899	16,860	12,782	13,653	13,772
^{226}Ra[c]	5,400	7,600	4,200	4,600	5,600	820	2300	5,000
TSS	202	282	500	62	520	210	898	0
Turbidity[d]	78	399	1160	17.4	192	45	164	0
TOC	<10	11.8	11.8	72	151	160	88	0
PW Type[f]	III	III	III	I	III	III	I	III

[a] Produced water from Barnett Shale (TX)

[b] dimensionless

[c] pCi/Liter

[d] Turbidity units: NTU

[e] adjusted to force ion balance (prior analyses found other anions were <1% of the chloride on a molar basis)

[f] Produced Water Type (see Figure 4 below for map of produced water types)

III. Current Processes for Produced Water Recovery

Figure 2 shows a schematic diagram of GEWPT's current mobile evaporation process for recovery of distilled water and a brine concentrate from produced water. In this figure, all quantities are based on the design case produced water composition. This is a very direct option for frac water recovery, including high-TDS produced waters that contain significant levels of ^{226}Ra and/or barium. This results in limited water recovery, but avoids generating solids with high ^{226}Ra or barium levels. Current methods for produced water pretreatment prior to thermal evaporation include oxidation and lime treatment, which precipitates iron and manganese and removes suspended solids[22,23]. Pretreatment for barium and radium is not required; barium and radium are carried along with the concentrate. Assuming that the concentrate leaving the evaporator has 300,000 mg/L TDS, 0.56 bbl of distilled water is recovered per bbl feed produced water for the design case. Table 3 shows the concentration factor and the cost of transportation and disposal of the concentrate, assuming transport from north-central Pennsylvania to Ohio and disposal by UIC in Ohio. The estimated cost for concentrate transportation from central Pennsylvania to Ohio and disposal by UIC is $11/bbl.

In lab experiments with Marcellus produced waters, the ^{226}Ra activity measured by gamma spectrometry in the pretreated produced water was identical to that of the untreated produced water, within the accuracy of the measurement. From this, we infer that the pretreatment sludge contains negligible ^{226}Ra activity.

The GEWPT mobile evaporator is currently undergoing field trials with produced water.

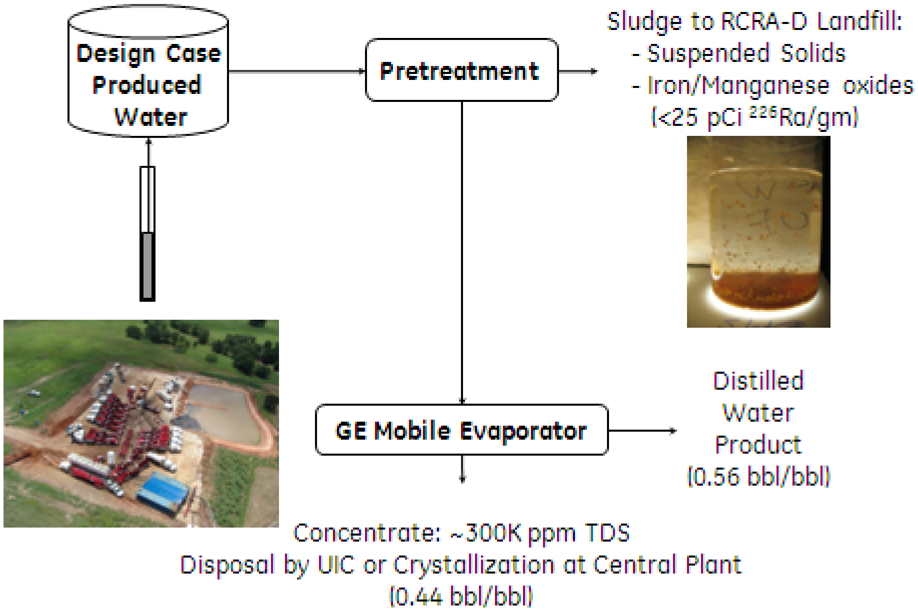

Figure 2. Current Produced Water Recovery Process (Design Case Produced Water Composition)

A. GEWPT Pilot-Scale Evaporator/Crystallizer Trials with Marcellus Produced Water

GEWPT conducted pilot-scale trials of Marcellus produced water evaporation in a vertical falling film evaporator and crystallization of the evaporator blowdown to generate a solid NaCl salt product and distilled water. Table 4 shows the composition of the evaporator feed (pretreated produced water) and the crystallizer feed. The crystallizer product passed TCLP and met ASTM D-635 standards for use as road deicing salt. Figure 3 contrasts the appearance of the original produced water, the distilled water product, and the recovered salt product.

Table 3. Produced Water Evaporation: Water Recovery

Well Number	1	2	3	4	5	6	7	Design Case
Feed TDS, mg/L	98,294	155,705	199,242	68,439	149,188	122,562	124,421	132,460
max water recovery: (wt H_2O)/(wt feed)[b]	0.902	0.844	0.801	0.932	0.851	0.877	0.876	0.868
Max water recovery: (vol H_2O)/(vol feed)	0.970	0.947	0.930	0.981	0.950	0.960	0.959	0.956
Evaporation only: fraction of maximum water recovery[c]	0.705	0.522	0.376	0.796	0.543	0.628	0.623	0.597
concentration factor, (Vol feed)/(Vol conc)	3.05	1.93	1.51	4.38	2.01	2.45	2.41	2.26
bbl distilled water/ bbl feed	0.700	0.513	0.365	0.793	0.535	0.622	0.616	0.590
Concentrate disposal cost[a], $/bbl feed	$3.93	$6.23	$7.97	$2.74	$5.97	$4.90	$4.98	$5.30

[a] Cost for transportation from north-central Pennsylvania to Ohio and UIC disposal in Ohio
[b] 100% dry salt product
[c] Concentrate: 300,000 mg/L TDS

Based on the measured barium concentration in the salt product and in the produced water, we estimated the produced water barium concentration for which the resulting barium concentration in a TCLP extract would equal 100 mg/L, the maximum value permissible under TCLP. The estimated value, $[Ba]_{max}$, is in the range of 1,000-2,000 mg Ba/L produced water.

Assuming that barium and radium behave identically in the NaCl crystallization process, we estimated the radium content in the solid salt product for a specified radium activity in the produced water. This assumption is based on the fact that the ionic radii of Ba^{+2} (1.49 Å) and Ra^{+2} (1.62 Å) are very similar, and that barium and radium behave essentially identically in all crystallization processes[24].

The design case produced water contains 5,000 pCi ^{226}Ra/liter. For this case, the estimated ^{226}Ra activity in the salt product is well below 10 pCi/gm.

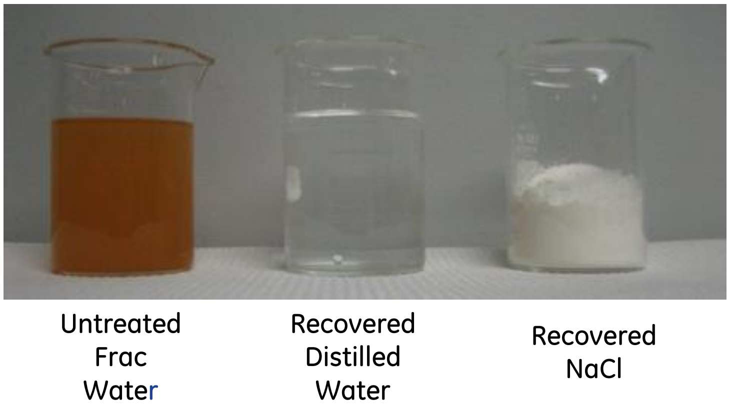

Figure 3. GEWPT Pilot Trial Results for Thermal Recovery of Water and Salt from Produced Water

This pilot test of produced water evaporation and crystallization demonstrates the feasibility of recovering distilled water and a salable salt product from produced water by thermal evaporation and NaCl crystallization. This pilot test also provides a basis for estimating $[Ba]_{max}$. These pilot results support the assertion that for the design case produced water (5,000 pCi $^{226}Ra/L$) as well as produced waters with significantly higher radium activities, the estimated radium activity in the product salt is well below the permissible level for disposal as nonhazardous waste in a RCRA-D landfill (<25 pCi $^{226}Ra/gm$ in PA) and is therefore negligible.

Table 4. Produced Water Composition for Pilot Evaporator and Crystallizer Test

(all quantities mg/L except where noted)

	Evaporator Feed	Crystallizer Feed
pH	6.0	5.9
TDS	122,000	271,000
Na^+	30,800	68,100
Fe^{++}	<0.5	<0.5
Mn^{++}	<0.2	<0.2
Cl^-	70,200	155,000
$SO_4^=$	<10	15
SiO_2	<10	42
TSS	None	None
Turbidity, NTU	<0.1	0.4

B. Produced Water Pretreatment Map

We developed the pretreatment map shown in Figure 4 based on the results of the produced water evaporation and crystallization pilot study conducted by GEWPT described above and sulfate precipitation material balance calculations (Section IV.C, below). This map identifies three "types" of produced water based on their barium concentrations and radium activities. The produced water compositions analyzed in this study are superimposed on this map. Each type of produced water requires a different pretreatment for barium removal prior to NaCl crystallization.

> Type I: The produced water barium concentration is below $[Ba]_{max}$ (a value in the range 1,000-2,000 mg/L) and is not restricted with respect to ^{226}Ra activity. Type I produced waters require neither barium nor radium removal prior to NaCl crystallization. Produced waters from Well-4 and Well-6 are of Type I.
>
> Type II: The produced water barium concentration is higher than $[Ba]_{max}$. Barium removal is needed prior to NaCl crystallization. Pretreatment of Type II produced water by sulfate precipitation yields a sulfate sludge that is safe for disposal in a RCRA-D landfill because the ^{226}Ra activity in the sludge is below the limit established by the state (25 pCi ^{226}Ra/gm sludge in PA). The location of the red line in Figure 4 depends on the RCRA-D limit for ^{226}Ra activity in a particular state. It is assumed that the sulfate sludge is 45 wt% solids.
>
> Type III: The produced water barium concentration is above $[Ba]_{max}$. Therefore, barium removal is needed prior to NaCl crystallization. Because the ^{226}Ra activity is above the red line in Figure 4, a pretreatment process other than direct sulfate precipitation must be used.

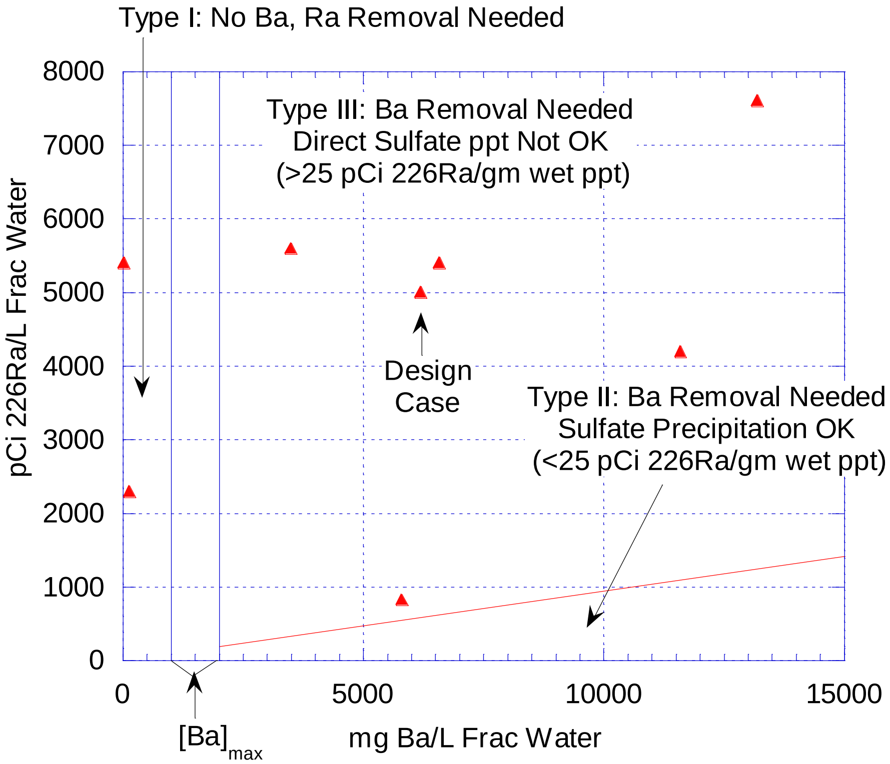

Figure 4. Map of Produced Water Types and Barium Removal Pretreatment Requirements (symbols represent produced water compositions analyzed in this study)

IV. Type III Produced Water Pretreatment Process Options

To recover distilled water and a salable salt from Type III produced waters, it is necessary to remove barium by a method other than direct sulfate precipitation. Sulfate precipitation for Type III produced waters would be acceptable if the radium is first removed from the produced water. We sought methods to selectively remove radium from produced water, including DOWEX™ RSC (radium specific complexer) resin. In Appendix I, we review the literature on RSC resins and show the results of laboratory screening of a variety of adsorbents for selective removal of radium from produced water. As described in Appendix I, of the 60 adsorbents that we screened, none was economically feasible. Therefore, we abandoned the effort to selectively remove radium from produced water.

As shown in Figure 5, we analyzed six processes for removal of barium, radium, and other multivalent cations from high-TDS brines. These include ion exchange, nanofiltration, sulfate precipitation, carbonate precipitation, the modified lime-soda process, and MnO_2 adsorption. Each process is reviewed in the following sections.

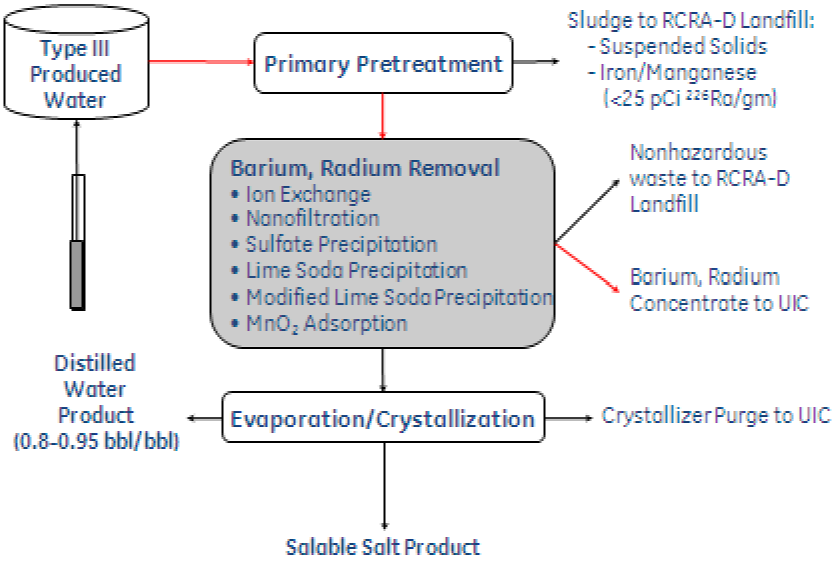

Figure 5. Schematic Diagram of Type III Produced Water Recovery Process and Pretreatment Options

A. Ion Exchange

As shown in Appendix II for the design case produced water, approximately one bed volume of chelating ion exchange resin is required to soften one bed volume of produced water. Thus, the ion exchange resin will be exhausted after it has processed one bed volume of produced water. The cost for regeneration chemicals and disposal of waste streams by UIC is calculated to be over \$6/bbl produced water. This cost is quite high, and it does not include the cost of sourcing or disposing of rinse water, which is needed after acid treatment and after caustic treatment. The regeneration rinse waters could most likely be combined, neutralized, and sent to an industrial wastewater treatment plant. Because of the high cost and need to handle significant volumes of rinse water, chelating ion exchange is not recommended for softening Marcellus produced water.

B. Nanofiltration

Appendix III shows simulation results for NF softening of produced water using WINFLOWS software from GEWPT. Produced waters from both the design case and Well-5 were considered. Maximum softened water (permeate) recovery calculations were based on a feed pressure upper limit of 600 psia. Table 5 shows the maximum permeate recovery calculated from the simulations for both cases.

Table 5. Nanofiltration: Simulation Results

	Well-1	Well-2	Well-3	Well-4	Well-5	Well-6	Well-7	Design Case
Maximum permeate recovery based on Winflows Simulation (%)					15			30

As noted above, the estimated cost for concentrate transportation from central Pennsylvania to Ohio and disposal by UIC is $11/bbl. For the design case produced water, the maximum permeate water recovery was 30%. At this recovery level, the transportation and disposal cost for the concentrate is $7.70 per bbl feed produced water. Based on the low recovery and the resulting high disposal cost of the concentrate, it is recommended that NF technology not be pursued for produced water softening.

C. Sulfate Coprecipitation of Barium and Radium

This section describes produced water pretreatment by sulfate precipitation and shows (through material balance calculations) that direct sulfate precipitation should not be utilized to pretreat Type III produced waters.

Sulfate precipitation is currently practiced for treating produced water. ProChemTech International, Inc. describes a chemical treatment process that pretreats produced water using three sequential precipitation steps[25]. The first step removes barium by precipitation as barium sulfate[26], which is non-leaching by TCLP. The subsequent precipitation steps remove the remaining scale formers. ProChemTech also describes a process in which produced water is treated with sulfuric acid to precipitate a barium sulfate sludge followed by lime/soda softening to generate a calcium carbonate sludge[27].

Veil[28] describes four commercial wastewater disposal facilities in Pennsylvania that, as of May, 2010, treated frac water and disposed of the treated water to either a POTW or a river under NPDES[29] permits. At these facilities, frac water is typically treated with sodium sulfate in order to precipitate barium, followed by lime treatment to precipitate magnesium and other hardness species. Precipitate from these steps is settled in a thickener and dewatered in a filter press. The sludge is sent to a local landfill.

Reserved Environmental Services[30] operates a 1.2 MGD produced water treatment facility in southwest Pennsylvania. TerrAqua[31] operates a 0.4 MGD facility in Williamsport, Pennsylvania. Both facilities remove barium, strontium, iron, and suspended solids from produced water and return the treated water to the customer for use in subsequent drilling and hydrofracturing operations. Because the sludge generated must pass TCLP, it is assumed that sulfate is used to precipitate barium and strontium as $BaSO_4$ and $SrSO_4$, respectively. Precipitation of barium and strontium with sulfate is attractive because sodium sulfate is relatively inexpensive ($130-160/short ton, anhydrous)[32], and $BaSO_4$ and $SrSO_4$ are nonhazardous. These plants may be expanded to include thermal evaporation and crystallization to yield a saleable salt product and distilled water. Additional frac water treatment plants are in operation in Pennsylvania. Dozens of additional treatment plants are in the planning stages and many have received permits[28].

a) Radium Solubility in Sulfate Environments

For radium-containing produced waters, sulfate treatment yields a coprecipitate of barium sulfate and radium sulfate (radio barite, $Ba(Ra)SO_4$), which is a solid solution of $RaSO_4$ and $BaSO_4$. Radio barite is well-known in the oil and gas industry. The EPA estimates that one-third of all domestic oil and gas wells produce some radium-contaminated scale[33]. Radium sulfate is one of the least water-soluble salts. The solubility of $RaSO_4$ alone in water is 4.8×10^{-8} M (11 ppb/w Ra, or 11×10^{6} pCi Ra/L)[34], which is about three orders of magnitude higher than the highest ^{226}Ra activity found in Marcellus produced water (10,000 pCi/L). However, the presence of barium reduces the radium sulfate solubility significantly. Doener and Hoskins[35], in 1925, confirmed that in the presence of sulfate ion, a solution of $RaCl_2$ and $BaCl_2$ coprecipitates as $RaSO_4$ and $BaSO_4$ even when the concentrations of Ra^{++} and $SO4^{=}$ are far below the solubility of $RaSO_4$ in water. They concluded that barium and radium coprecipitate to form a solid solution of $RaSO_4$ and $BaSO_4$. Under ideal solid solution conditions, the *calculated* solubility[36] of $RaSO_4$ in equilibrium with a solid solution of $(Ra,Ba,Ca,Sr)SO_4$ is 7×10^{-13} M, or 2×10^{-7} ppm/w[37] Ra. This calculated solubility of Ra is equivalent to 200 pCi/L of ^{226}Ra. In GEGR laboratory experiments with Well-3 produced water, the radium activity in solution after addition of an excess of sodium sulfate (vs. barium) was non-detectable by high purity germanium (HPGe) gamma spectrometry. The detection limit for ^{226}Ra was 17 pCi/liter.

b) Material Balance for Barium and Radium Sulfate Precipitation

As noted above, sulfate sludge may be safely and economically disposed of as nonhazardous solid waste in a RCRA-D landfill if the ^{226}Ra activity in the sludge is below 5-50 pCi/gm. The limit varies by state and is 25 pCi/gm for Pennsylvania. The cost for sludge disposal as nonhazardous waste in a RCRA-D landfill is typically about $50/ton. Sludge that exceeds this value must be disposed of as Low Level Radioactive Waste (LLRW). Energy Solutions, Inc. (Utah) charges about $200/ft^3 (excluding transportation) for disposal of Class A LLRW, which can contain up to 10 nCi/gm ^{226}Ra.

We conducted a simple material balance to estimate the radium activity in the (Ba,Ra)SO_4 sludge. We assumed that on addition of a stoichiometric amount of Na_2SO_4 to produced water, *all* the barium and radium in the raw produced water precipitate as (Ba,Ra)SO_4 sludge, and that no other components precipitate. We also assumed that the sludge would be dried to 45% solids before being transported to a landfill. Figure 6 shows the calculated radium activity in the wet sludge as a function of the radium activity in the produced water feed for six levels of barium in the produced water [38]. Design case produced water contains 6,200 mg barium/L. For this barium concentration, the produced water ^{226}Ra activity must be below about 600 pCi/L for the resulting sulfate sludge to meet Pennsylvania's RCRA-D disposal criteria. For all produced waters analyzed in this study, the calculated ^{226}Ra activity in a hypothetical (Ba,Ra)SO_4 sludge is above 25 pCi/gm, as shown in Table 6. Therefore, the sulfate sludge would need to be either blended with sufficient non-radioactive solid waste to meet the RCRA-D specification for ^{226}Ra activity or treated as LLRW.

Table 6 also shows the amount of wet sulfate sludge generated per barrel of produced water, as well as the cost of disposing of this sludge as LLRW. The cost of sludge disposal as LLRW is prohibitive. Because Well-4 and Well-7 are Type I produced waters, they do not need pretreatment for barium removal prior to NaCl crystallization.

Table 6. Material Balance for $BaSO_4$-$RaSO_4$ Sludge (45 wt% solids)

Well Number	1	2	3	4[a]	5	6	7[a]	Design Case
^{226}Ra Activity in wet Sludge, pCi/gm	217	152	95.9	-	424	37.4	-	213
Wet Sludge quantity lb/bbl Produced Water	8.71	17.5	15.4	-	4.63	7.68	-	8.21
LLRW Disposal Cost $/bbl Produced Water	$18	$36	$32	-	$10	$16	-	$17

[a] Type I produced water

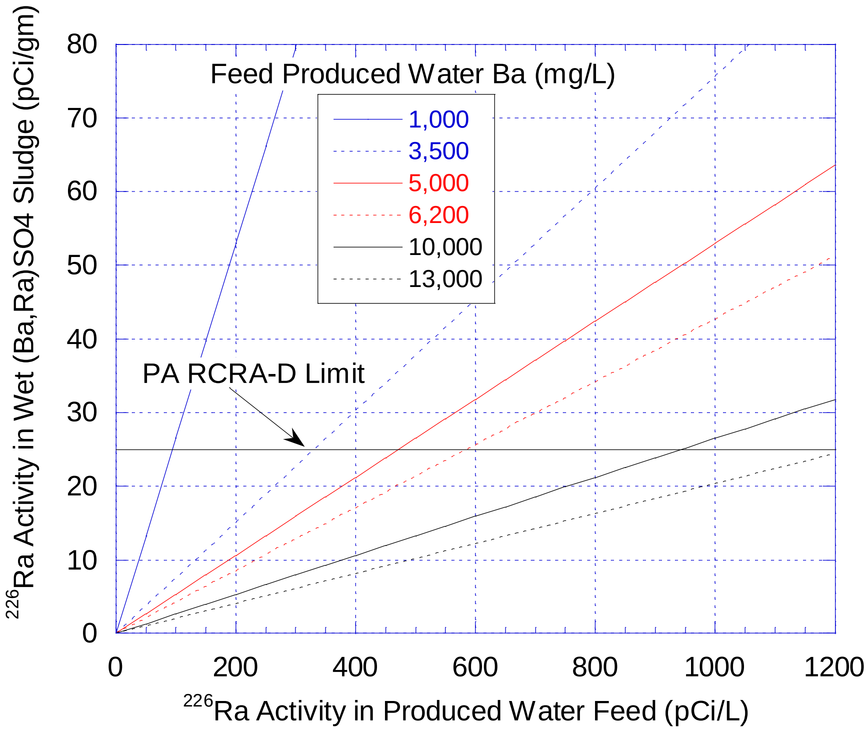

Figure 6. Calculated Sludge ^{226}Ra Activity for (Ra,Ba)SO_4 Coprecipitation

D. Lime-Soda Precipitation

Treating produced water with lime and sodium carbonate precipitates magnesium as $Mg(OH)_2$ and calcium, strontium, barium, and radium[39] as their corresponding carbonates. Table 7 shows, for each produced water, the calculated ^{226}Ra activity for the wet carbonate sludge resulting from complete softening by lime-soda treatment (sludge: 45 wt% solids). Each of these activities is higher than the maximum level permitted for RCRA-D disposal in Pennsylvania. These sludges would have to be disposed of as LLRW, and the cost for disposal would be prohibitive.

Table 7. Calculated Barium Concentration and ^{226}Ra Activity in Wet Carbonate Sludge for Lime-Soda Treated Produced Waters (45% solids)

Well Number	1	2	3	4	5	6	7	Design Case
pCi ^{226}Ra/gm wet sludge	87.2	64.7	31.4	143.2	56.9	10.3	31.2	58.0
Ba in wet sludge, ppm/w	106K	112K	86.6K	848	35.5K	72.6K	2.00K	80.0K
LLRW Disposal cost, $/bbl	$45	$86	$98	$28	$72	$59	$54	$63
Produced Water Type	III	III	III	I	III	III	I	III

In addition, barium carbonate is easily leached with acid, and sludge that yields above 100 mg barium/L in a TCLP extract will not pass TCLP. Table 7 shows that for all Type III produced waters, the barium concentration in the precipitate is far too high to be suitable for disposal in a RCRA-D landfill. Thus, lime-soda softening and sludge disposal of Type III produced water is not practical.

E. Modified Lime-Soda Process

1. Introduction

Table 8 shows the costs of disposal and restrictions on ^{226}Ra activity for three disposal options for pretreatment process byproducts. The low disposal cost by UIC for waste that contains ^{226}Ra is a strong motivation to develop a process that yields an aqueous ^{226}Ra (and barium) concentrate. According to the Ohio Department of Natural Resources, which manages the underground injection control (UIC) program, there is currently no official limitation on the ^{226}Ra activity or barium concentration in liquids disposed of by UIC. In addition, disposal by UIC is regarded as a safe method to avoid groundwater or aquifer contamination.

Table 8. Disposal Costs (excluding transportation)

	RCRA-D Nonhazardous Landfill	UIC (Deep-well Injection)	Low-Level Radioactive Waste (LLRW)
Locations	50 sites in PA	Ohio, WV	Utah
Maximum ^{226}Ra pCi/gm	25 (in PA)	-	10,000
Disposal cost: $/short ton	50	11.5	6,400

Figure 7 shows a schematic diagram of the modified lime-soda process to pretreat Type III produced water. Produced water is first oxidized and contacted with lime to precipitate magnesium as $Mg(OH)_2$, iron as $Fe(OH)_3$, and manganese as MnO_2. Just over 1 mole $Ca(OH)_2$ per mole Mg results in essentially complete precipitation of Mg as $Mg(OH)_2$. The pH in Precipitation Stage 1A is about 10.6-10.8. Sodium carbonate is then added to selectively precipitate calcium and strontium. The pH in Precipitation Stage 1B is about 11-11.3. Precipitation Stages 1A and 1B may be conducted in a single vessel. The precipitates from Stages 1A and 1B are nonhazardous and may be disposed of in a RCRA-D nonhazardous landfill.

In Precipitation Stage 2, the produced water is treated with additional sodium carbonate to precipitate both barium and radium as carbonates. The Stage 2 precipitate is removed from the produced water and treated with concentrated HCl to convert $BaCO_3$ and $RaCO_3$ to CO_2, $BaCl_2$, and $RaCl_2$. Carbon dioxide is vented to the atmosphere, optionally though a carbon adsorbent to trap radon gas. The HCl addition is adjusted to achieve a pH low enough to strip essentially all of the carbonates from the aqueous concentrate stream (e.g. pH 2-4). This concentrate stream may be neutralized if desired prior to disposal by UIC.

After Precipitation Stage 2, the softened produced water still contains a significant concentration of dissolved carbonates (about 450 ppm/w $CO_3^{=}$ for design case produced water). HCl is added to this stream to drive off CO_2. The softened, decarbonated produced water may then be thermally treated to recover distilled water and a solid salt product.

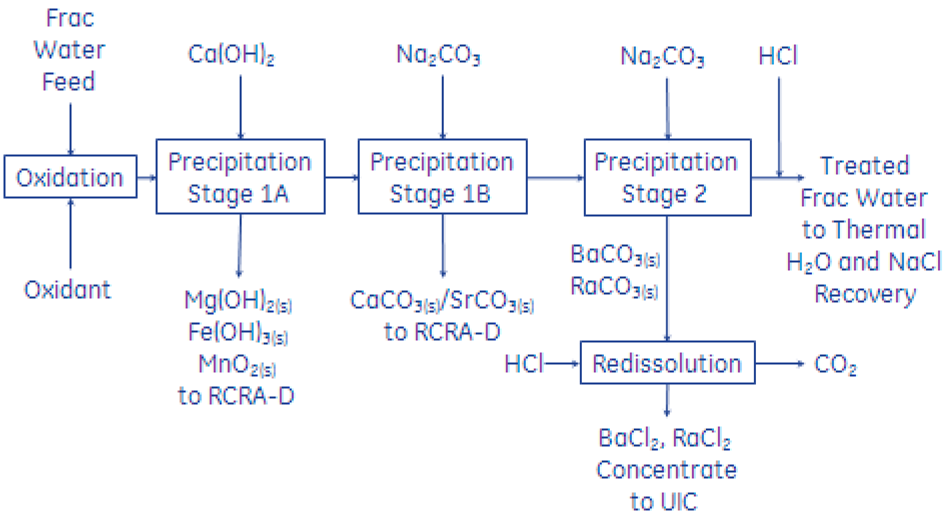

Figure 7. Schematic Diagram of Modified Lime-Soda Process

This process exploits the relative solubilities of the Group II metal carbonates. Table 9 shows that calcium and strontium carbonate are less soluble than either barium or radium carbonate and are thus expected to precipitate preferentially over barium and radium carbonate as sodium carbonate is added to the system.

The produced water pretreated by this process is essentially completely softened. This enables very high water and NaCl recoveries. Further, the relatively pure salt product may be usable for higher value applications than road deicing. For example, the salt product may be used as feedstock for caustic and chlorine production or for industrial water softening.

Table 9. Water Solubility of Group II Metal Carbonates[40]

Species	Solubility, gm/100 gm H_2O	Temperature, °C
$MgCO_3.5H_2O$	0.176	7
$MgCO_3$	0.0106	~20
$CaCO_3$ (calcite)	0.0014	25
$CaCO_3$ (aragonite)	0.00153	25
$SrCO_3$	0.0011	18
BaCO3-alpha	0.002	20
$BaCO_3$-beta	0.022	18
$BaCO_3$-gamma	0.0022	18
$RaCO_3$	more soluble than barium carbonate[24]	

2. Aspen Plus®/OLI Simulations

We conducted Aspen Plus®/OLI simulations of the modified lime-soda process. Figure 8 shows simulation results for the design case. Prior to Na_2CO_3 addition, the magnesium has been essentially completely precipitated by lime addition. This figure shows that as Na_2CO_3 is added to the system, $CaCO_3$ precipitates first, followed by coprecipitation of both $CaCO_3$ and $SrCO_3$.

Barium carbonate does not begin to precipitate until the calcium and strontium have been nearly completely precipitated. At about 1.15 times the stoichiometric amount of Na_2CO_3, the barium precipitation is essentially complete. At this point, the solution contains about 50 ppm/w Ba (compared with over 5600 ppm/w in the feed solution). The target barium concentration in Precipitation Stage 2 may be defined through additional laboratory and pilot testing. Appendix IV shows precipitation plots for each of the produced waters characterized in this study.

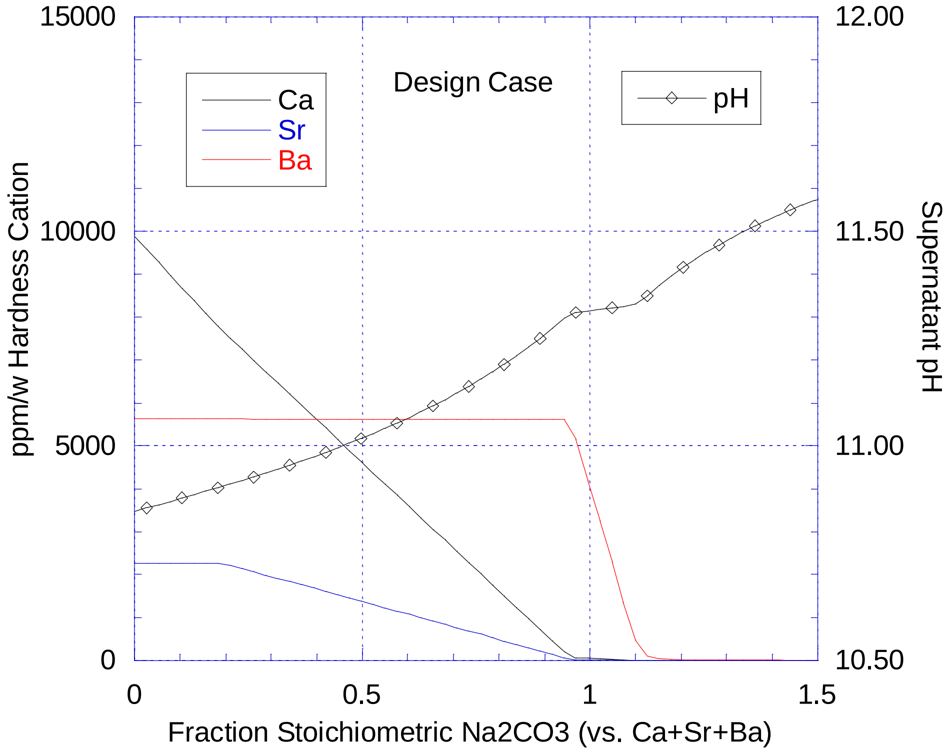

Figure 8. Simulation Results for Modified Lime-Soda Process: Design Case

3. Modified Lime-Soda Pretreatment Process Cost Calculations

Table 10 shows the calculated chemical and disposal costs for the produced waters considered in this study. Table 10 reports both a minimum and maximum cost estimate for each produced water considered in this study. The *minimum* cost assumes that in both Precipitation Stages 1A-1B, and Precipitation Stage 2, equilibrium conditions prevail. Under equilibrium conditions, negligible amounts of barium and radium precipitate in Stages 1A-1B along with the magnesium, calcium, and strontium. Similarly, negligible amounts of magnesium, calcium, and strontium precipitate in Stage 2. For the design case produced water, the minimum cost for chemicals and disposal is \$3.5/bbl produced water feed.

The *maximum* cost is based on no selectivity in the carbonate precipitation process. Thus, Precipitation Stages 1B and 2 are combined. Calcium, strontium, barium, and radium precipitate together as a single mixture. In this case, no carbonates are disposed of as RCRA-D waste. All carbonates are treated by HCl to generate a chloride concentrate for UIC disposal.

For the design case produced water, the maximum cost for chemicals and disposal is $5.8/bbl produced water feed.

Table 10. Chemical and Disposal Costs for Modified Lime-Soda Process

Well Number	1	2	3	4	5	6	7	Design
Feed TDS, mg/L	98,294	155,705	199,242	68,439	149,188	122,562	124,421	132,460
Hardness as Ca^{++}, mg/L	9,167	17,196	20,727	6,899	16,860	12,782	13,653	13,772
Feed Ba, mg/L	6,580	13,200	11,600	32	3,500	5,800	147	6,200
lb dry $Ca(OH)_2$/bbl PrW[a]	0.489	0.918	1.45	0.589	1.01	0.870	1.24	0.876
lb dry Na_2CO_3/bbl PrW	8.56	16.8	21.0	6.71	14.9	14.6	13.1	13.2
Case 1: 100% Carbonate Precipitation Selectivity (Minimum Cost)								
lb dry HCl/bbl PrW	1.44	2.95	2.91	0.288	1.25	2.50	0.285	1.51
Chemicals & Disposal $/bbl Produced Water	$2.45	$4.87	$5.78	$1.54	$3.77	$3.89	$2.98	$3.50
bbl UIC disposal/bbl PrW	0.0307	0.0633	0.0606	$3.3x10^{-5}$	0.0251	0.0301	$5.2x10^{-4}$	0.0305
lb wet solids to RCRA-D/ bbl Produced Water	15.0	28.8	38.6	14.3	29.8	23.1	29.0	25.2
Case 2: 0% Carbonate Precipitation Selectivity (Maximum Cost)								
lb dry HCl/bbl PrW	5.68	11.1	13.78	4.19	9.94	8.07	8.60	8.74
Chemicals & Disposal $/bbl Produced Water	$3.84	$7.53	$9.37	$2.93	$6.67	$6.09	$5.84	$5.91
bbl UIC disposal/bbl PrW	0.0944	0.185	0.227	0.0664	0.161	0.132	0.133	0.143
lb wet solids to RCRA-D/ bbl Produced Water	0.83	1.59	2.51	1.01	1.74	1.47	2.14	1.49

[a] PrW: Produced water

4. Laboratory Tests of Modified Lime-Soda Process

We conducted two exploratory laboratory experiments to test the modified lime-soda process and one experiment in which NaOH was substituted for Na_2CO_3 during Precipitation Stages 1A and 1B. Appendix IV shows the details of these experiments. In each of the first two experiments, a sample of produced water was added to a beaker and first treated with lime, followed by addition of Na_2CO_3, either portionwise or continuously. Samples of the supernatant were filtered and analyzed for residual radium by Liquid Scintillation Counting (LSC). For a given sample, the radium activity is proportional to the measured counts per minute (CPM). Results are reported as the fraction of the produced water CPM remaining in solution after a specific amount of Na_2CO_3 has been added. Since barium and radium coprecipitate as carbonates, it is assumed that the fraction barium remaining in solution is approximately equal to the fraction radium remaining in solution[24].

Ideally, the fraction radium activity remaining in solution is unity until the number of moles of Na_2CO_3 added equals the number of moles of Ca^{++} + Sr^{++} in the feed solution, followed by a decrease to zero as the number of moles to Na_2CO_3 increases to about 1.15 times the number of moles of Ca^{++} + Sr^{++} + Ba^{++} initially in the produced water. The 15% molar excess carbonate value is based on the simulation results for Well-5 produced water. According to the simulation, with 15% molar excess Na_2CO_3 addition, the residual barium concentration in solution is 59 ppm/w, which corresponds to a reduction of about 99% vs. feed concentration.

a) Experiment 20110826 with Well-5 Produced Water

We added one liter of Well-5 produced water and a magnetic stir bar to a beaker. After $Ca(OH)_2$ addition, Na_2CO_3 was added to the agitated mixture in ten equal portions. Enough Na_2CO_3 was added to precipitate all of the calcium, strontium, and barium. Each portion was added essentially instantaneously. Approximately two minutes elapsed between Na_2CO_3 additions.

Instead of the ideal behavior, Figure 9 shows that the fraction feed CPM decreased *monotonically* with increasing Na_2CO_3 addition. This suggests that barium and radium precipitated in proportion to the amount of Na_2CO_3 addition. Thus, under these conditions, the process showed no selectivity for the less soluble carbonates (Ca, Sr) over barium and radium. It is hypothesized that the Na_2CO_3 addition rate was too high (for the mixing intensity afforded by the magnetic stir bar) for near-equilibrium conditions to apply.

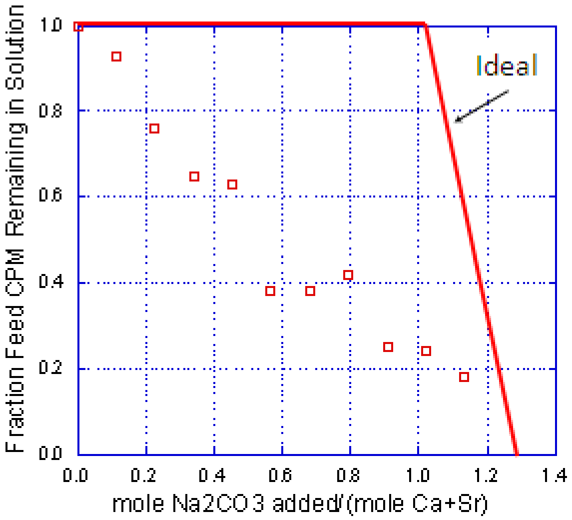

Figure 9. LSC Results for Experiment 20110826

b) Experiment 20110901 with Well-5 Produced Water

Experiment 20110826 was repeated with addition of a solution of Na_2CO_3 to an agitated mixture of Well-5 produced water at a constant rate over the course of 316 minutes. Figure 10 shows the results of this experiment. Although the ideal behavior was not achieved, this experiment shows that steady, slower Na_2CO_3 addition resulted in much better selectivity than observed in experiment 20110826. Additional tests are planned with improved agitation and other techniques to more closely approach ideal behavior.

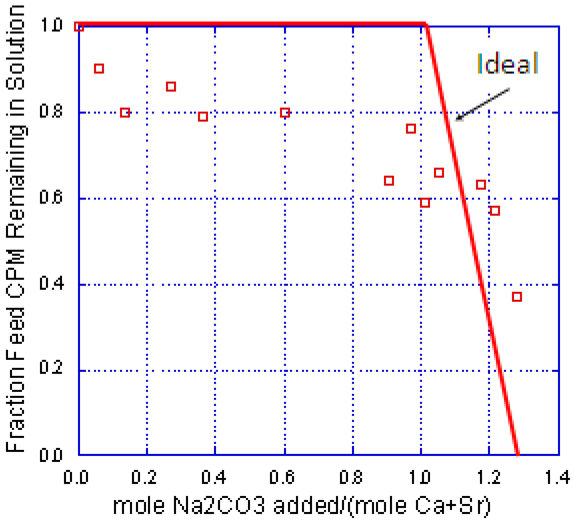

Figure 10. LSC Results for Expt 20110901

c) Experiment 20110708 with Well-5 Produced Water

This test utilized NaOH to precipitate Mg, Ca, and Sr as the corresponding hydroxides, followed by Na_2CO_3 to precipitate Ba and Ra as the carbonates. This approach is based on the relatively high solubility of $Ba(OH)_2$ (5.6 gm $Ba(OH).8H_2O$ per 100 gm H_2O at 15°C[40]), which serves to keep barium and radium in solution while magnesium, calcium, and strontium precipitate as hydroxides.

NaOH was added portionwise to a beaker of Well-5 produced water and the supernatant was sampled after each aliquot for LSC analysis. After the last NaOH addition, the slurry was filtered through a 1μ glass filter. The filtrate was placed back into the beaker and the agitation was restarted. Then a series of six portions of Na_2CO_3 was added in the same manner, with sampling after each portion.

Figure 11 shows the results of this experiment. Here, the barium and radium remain in solution throughout the course of the NaOH addition. The total amount of NaOH was sufficient to precipitate all of the magnesium, calcium, and strontium. Although excess Na_2CO_3 was added, more Na_2CO_3 may be necessary to completely precipitate the barium and radium as carbonates. This can be determined with further experimental and simulation studies. Although this process shows better selectivity toward Group II metals other than barium and radium in the first step, the cost of NaOH per equivalent is about 30% higher than the cost of Na_2CO_3 per equivalent. Further, the precipitate obtained from the NaOH addition was very difficult to filter.

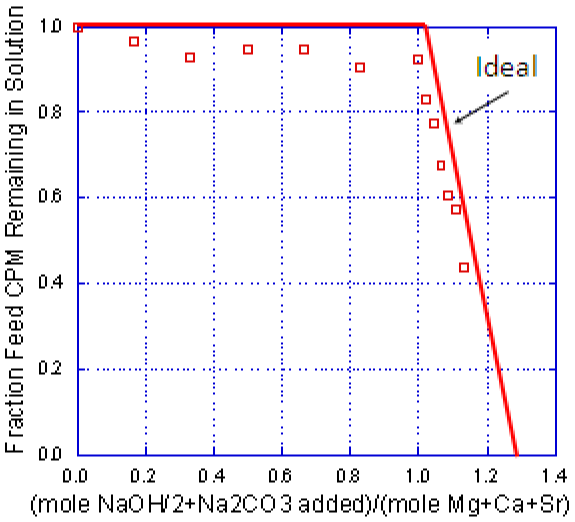

Figure 11. LSC Results for Experiment 20110708

F. MnO_2 Barium and Radium Adsorption Process

We identified MnO_2 as an effective adsorbent for barium and radium removal from produced water. We tested MnO_2 adsorbents that were made at Pacific Northwest National Laboratory (PNNL) and obtained from commercial sources.

We also demonstrated that barium and radium can be stripped from these adsorbents using dilute HCl. This concentrate of $RaCl_2$ and $BaCl_2$ can be disposed of by UIC. We showed that regenerated MnO_2 adsorbent is effective for reuse. Alternatively, HCl-treated adsorbent can be rinsed and disposed of as nonhazardous solid waste as long as it meets RCRA-D disposal criteria. On the basis of the materials and disposal costs, this process is less expensive than the modified lime-soda process. However, for adsorbents that have commercially practical barium and radium capacity in produced water applications, the particle size is in the micron or submicron range. Additional development is required to define cost-effective methods of particle handling. Suitable methods must be developed for contacting the particles with produced water, filtering the particles from the treated produced water, and recovering the particles for HCl treatment and disposal. This process is currently under development at GEGR.

1. MnO_2 Characterization and Capacity Screening

For adsorbent capacity screening studies, we measured the radium capacity of each adsorbent by LSC. Adsorption experiments were also conducted in which both barium and radium capacities were measured. These experiments, in substantial agreement with an earlier study by Moon et al[41], showed that MnO_2 adsorbs comparable *percentages* of both barium and radium from solution.

We measured the ^{226}Ra adsorption capacity of both commercially available MnO_2 powder (Fluka Activated MnO_2) and 14 proprietary MnO_2 adsorbents obtained from PNNL. All materials in this study were powders. The Fluka activated MnO_2 was pure MnO_2 powder. Each PNNL material was characterized by BET for surface area and by Energy Dispersive Spectroscopy (EDS) for bulk composition. As shown in Table 11, the materials from PNNL comprise various forms of MnO_2 supported on silica. These materials are referred to as “resins”.

We first screened the PNNL materials for their ^{226}Ra capacity using Well-4 produced water. Even though Well-4 produced water is Type I, it was useful for these studies because it afforded significant ^{226}Ra capacity to each adsorbent, which enabled the use of LSC for capacity measurements. Table 11 shows that PNNL samples C, D, F, G, I, K, and L have the highest ^{226}Ra capacities.

We also evaluated the adsorption and regeneration performance of material “C” for both ^{226}Ra and barium. For these studies, we measured ^{226}Ra activity by LSC and barium concentration by ICP.

2. MnO_2 Regeneration Process

We conducted nine adsorption-regeneration tests with Fluka activated MnO_2, using Well-4 produced water and HCl for regeneration. These tests focused on defining regeneration process conditions. The performance of a given regeneration condition was measured by both the amount of ^{226}Ra removed from the adsorbent and the amount of ^{226}Ra capacity in the next adsorption cycle, as measured by LSC.

Table 11. Characterization of PNNL Adsorbents

Resin: PNNL-	BET Area, m^2/gm	Principal Components (EDS)	^{226}Ra Capacity, pCi/gm resin with Well-4 produced water	Morphology
A	32.1	Mn	69	~100 μ, multi-faceted particles; very little fine structure
B	<30	Mn	13	
C	203	Mn, Si support, K	**2350**	Aggregates of ~100 nM particles; high surface area
D	75.7	Mn, Si support, K	**2165**	
E	74.9	Fe	102	
F	54	Mn, Fe	**2015**	
G	280	Mn, Si support	**2620**	
H	69.7	Fe	5	
I	96.0	Mn, Fe	**2120**	
J	82.6	Fe	619	
K	149.2	Mn, Fe	**2130**	
L	95.2	Mn, Fe	**2220**	
M	107.7	Mn, Fe	253	
N	65.82	Mn, Fe	419	

Each MnO_2 sample went through four complete adsorption-regeneration cycles, followed by a fifth adsorption capacity test. The regeneration experiments utilized either 0.01N, 0.1N, or 1.0N HCl. These tests covered a factor of 400 in the amount of regeneration HCl per gram MnO_2 (0.2-80 mmol HCl per gm MnO_2).

Figure 12 shows the performance of Fluka activated MnO_2 with respect to ^{226}Ra adsorption and regeneration. The adsorption behavior was essentially unchanged from cycle-to-cycle, but surprisingly, the regeneration effectiveness increases in each subsequent cycle.

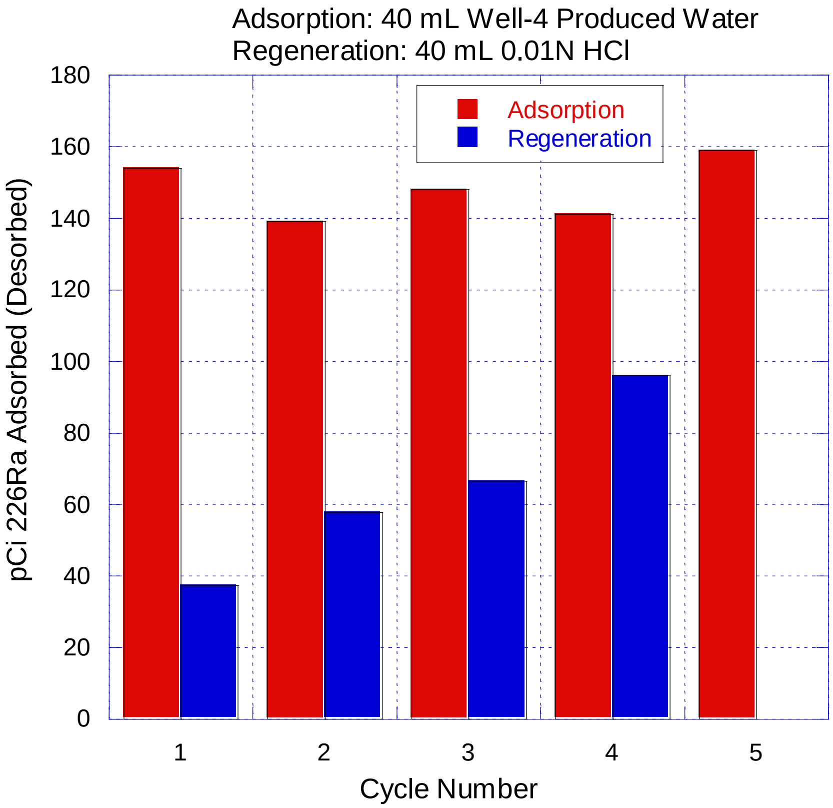

Figure 12. Adsorption and Regeneration Study for Fluka Activated MnO_2

Figure 13 shows the effect of regeneration HCl usage on the effectiveness of the regeneration for each of the four regeneration cycles. The amount of ^{226}Ra regenerated (desorbed) from MnO_2 is roughly proportional to the log of the regeneration HCl usage, and is essentially independent of the HCl concentration. The results of Figure 13 suggest that 2-4 mmol HCl per gm MnO_2 is effective for regenerating the MnO_2 used in these tests.

The regeneration effectiveness may also be measured by the amount of ^{226}Ra that is adsorbed by the resin on Cycle 5. Figure 13 shows this value plotted against the regeneration HCl usage (mmol HCl/gm MnO_2). These results suggest that 0.8 mmol HCl per gram MnO_2 is sufficient to fully regenerate MnO_2, even though at this loading the amount of ^{226}Ra desorbed (96 pCi in Cycle 5) is only about 60% of the amount adsorbed. Additional testing will be needed to define an HCl treatment that enables tens or hundreds of adsorption-regeneration cycles.

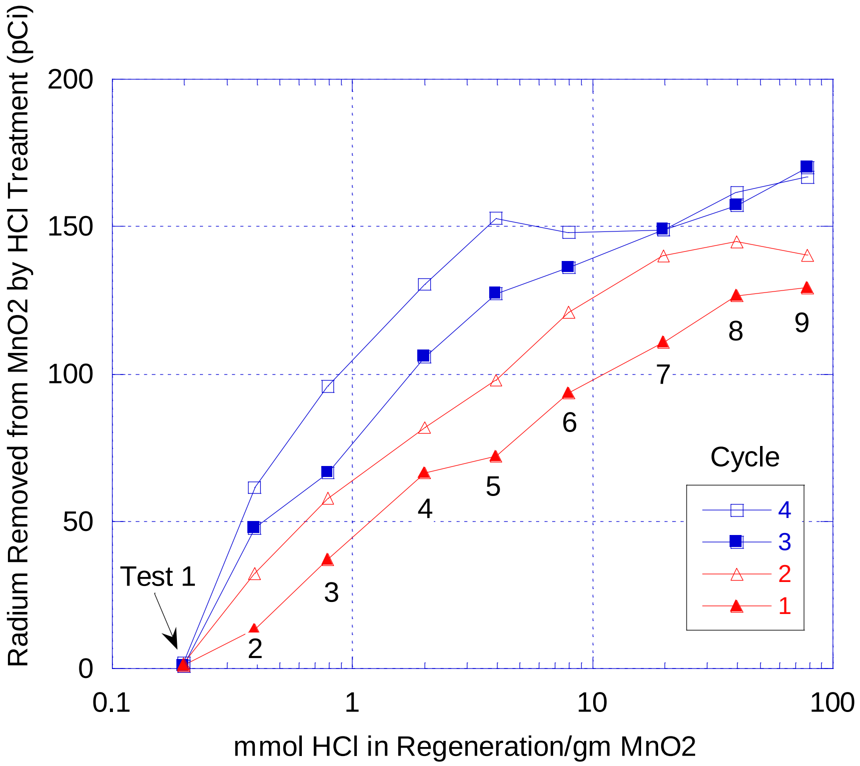

Figure 13. Effect of Regeneration HCl on Radium Removal Effectiveness

3. PNNL-C Adsorbent Capacity and Regenerability

We conducted a series of experiments to test the adsorption capacity and regenerability of PNNL-C adsorbent. Table 12 shows the overall performance of PNNL-C adsorbent for both barium and ^{226}Ra adsorption and regeneration by HCl. We used Well-4 produced water in each loading cycle and 0.1N HCl as a regenerant. For a regeneration control, we used DI H_2O. Experiments 10-12 utilized one batch of PNNL-C adsorbent; Experiment 13 utilized a second, larger, batch of PNNL-C adsorbent.

Table 12 shows that in these tests, the PNNL-C adsorbent removed about 70-80% of the ^{226}Ra and about 34-72% of the barium from the Well-4 produced water. These results show that the PNNL-C adsorbent is only slightly selective toward radium over barium. The same behavior was observed for Fluka MnO_2. Moon et al[41] found no difference in selectivity between radium and barium for adsorption onto MnO_2.

Regeneration with 0.1N HCl removed about 37-55% of the ^{226}Ra and about 81-96% of the barium that was adsorbed during the adsorption cycle. In contrast, DI H_2O removed only 5% of the adsorbed ^{226}Ra and 9% of the barium that was adsorbed. Based on these experiments, MnO_2 is effective for both barium and radium adsorption from Well-4 produced water; 0.1N HCl is effective for regenerating both barium and radium from MnO_2.

Table 12. Summary of Adsorption-Regeneration Tests with PNNL-C MnO_2 Adsorbent

Test	Regenerant	^{226}Ra capacity, pCi/gm adsorbent	Fraction ^{226}Ra adsorbed by MnO_2	Fraction adsorbed ^{226}Ra removed by regen	Ba capacity, mg/gm adsorbent	Fraction Ba adsorbed by MnO_2	Fraction adsorbed Ba removed by regeneration
10	0.1N HCl	3,240 3,490[a]	0.76 0.82	0.55	15	0.50 0.72	0.96
11	DI H_2O	3,300 2,880[a]	0.77 0.68	0.05	15	0.50 0.34	0.093
12	0.1N HCl	3,150	0.74	0.37	15	0.50	0.81
13	0.1N HCl	3,460	0.81	0.40	16	0.52	0.83

[a] Tests 10 and 11 utilized two adsorption cycles, with a regeneration step between the two cycles. The first value is for the first cycle; the second value is for the second cycle.

4. MnO_2 Barium and Radium Adsorption-Regeneration Process

Figure 14 shows a schematic diagram of a hypothetical process for adsorbing barium and radium from produced water onto MnO_2, regenerating the MnO_2 with HCl to generate a $BaCl_2$-$RaCl_2$ concentrate, and disposing of the $BaCl_2$-$RaCl_2$ concentrate solution by UIC. It is anticipated that a fraction of the MnO_2 inventory would be continuously or periodically removed from the separation step following adsorption and regeneration. This regenerated, "spent MnO_2", may be disposed of as nonhazardous solid waste in a RCRA-D landfill, assuming that the barium concentration and ^{226}Ra activity meet RCRA-D disposal criteria.

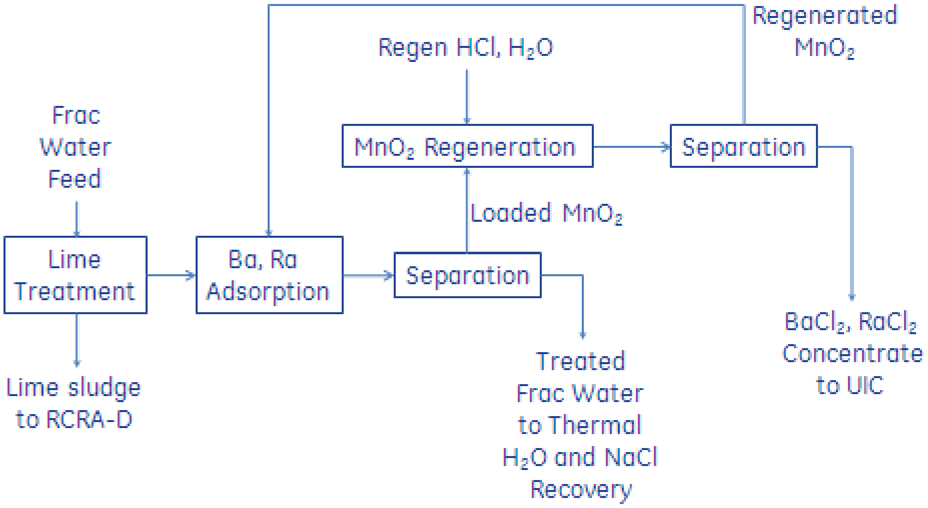

Figure 14. Schematic Diagram of MnO_2 Barium and Radium Adsorption-Regeneration Process

Figure 15 shows a schematic diagram of a hypothetical regeneration process for MnO_2 adsorbent. A concentrated solution of $BaCl_2$ and $RaCl_2$ in dilute HCl is recirculated over the loaded MnO_2 to desorb $RaCl_2$ and $BaCl_2$. Concentrated HCl is added to the loop to maintain an HCl concentration of about 0.1M. The stripped MnO_2 is rinsed with water, and returned to the adsorption process. The rinse water and a purge stream from the $BaCl_2$-$RaCl_2$-acid loop are combined and neutralized with NaOH for disposal by UIC.

Based on the results shown in Table 12, approximately equal percentages of barium and ^{226}Ra adsorb from Well-4 produced water onto MnO_2 and desorb via HCl displacement from MnO_2. For the design case produced water composition, the concentration of ^{226}Ra is 5,000 pCi/liter (5×10^{-6} mg/L). The concentration of barium is 6,200 mg/L. Thus, the concentration of barium is nine orders of magnitude greater than the concentration of radium. Therefore, the materials and disposal costs are estimated based only on the barium concentration in the produced water.

We estimated the materials and disposal costs for this process for the design case produced water. The materials cost for MnO_2 synthesis is based on a standard preparation for manganese oxide shown in equation (1). Manganese sulfate can be used in place of manganese chloride, as shown in equation (2).

$$2KMnO_4 + 3MnCl_2 + 4KOH \rightarrow 5MnO_2 + 6KCl + 2H_2O \qquad (1)$$

$$2KMnO_4 + 3MnSO_4 + 4KOH \rightarrow 5MnO_2 + 3K_2SO_4 + 2H_2O \qquad (2)$$

In addition, we made the following assumptions.

- 2.5 moles of HCl are required per mole of barium to remove barium during regeneration.
- Stripped MnO_2 is rinsed with twice its volume of clean water.
- The purge from the regeneration loop and the rinse stream are combined and neutralized with 2.5 moles of NaOH per mole barium.
- The neutralized mixture is disposed of by UIC.

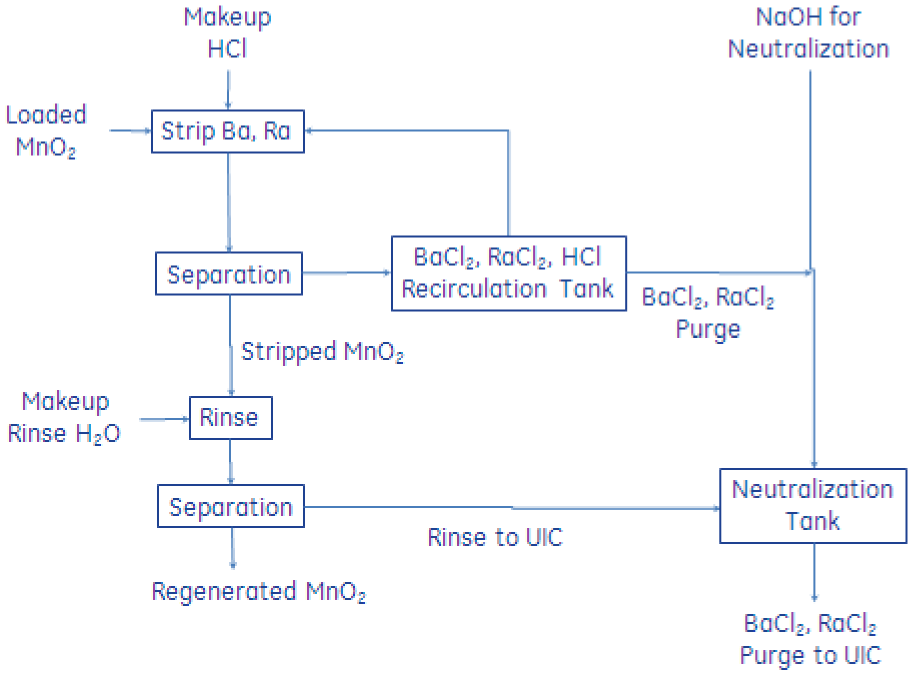

Figure 15. Schematic Diagram of MnO_2 Regeneration Process

Table 13 shows the estimated costs for synthesis and regeneration of an MnO_2-based adsorbent for barium and radium adsorption from produced water for the design case. The MnO_2 is assumed to be usable for 5 adsorption-regeneration cycles. The estimated barium capacity is based on the distribution coefficient of 2,800 reported by Moon[41] for both radium and barium adsorption on MnO_2 resin. Based on equation (3), below, and a final barium concentration in the treated produced water of 500 mg/L, the calculated barium capacity is approximately 1,400 mg/gm MnO_2. To be conservative, we assumed a barium capacity of 1,000 mg/gm MnO_2.

$$K_d = \frac{\left(\dfrac{mg\ Ba\ on\ MnO_2}{gm\ MnO_2} \right)}{\left(\dfrac{mg\ Ba\ in\ solution}{gm\ solution} \right)} = 2800 \qquad (3)$$

Figure 16 shows the estimated cost for chemicals and disposal for the MnO_2 adsorption-regeneration process as a function of the number of cycles for which the adsorbent is effective. In this figure, the final barium concentration refers to the barium concentration of the treated produced water leaving the MnO_2 adsorption step. For an adsorbent lifetime of 10 cycles, and a treated produced water barium concentration of 500 mg/L, the materials and disposal cost for barium and radium removal and disposal is $1.7/bbl produced water. For this case, the waste volume for UIC disposal is 0.05 bbl/bbl produced water.

Table 13. Cost of Materials and Disposal:
MnO_2 Barium and Radium Adsorption-Regeneration Process
(Design Case Produced Water; 5 Adsorption-Regeneration Cycles)

Cost item	Usage/bbl produced water	$/bbl produced water
MnO_2 adsorbent consumption	180 gm	$1.19
Disposal of spent adsorbent (MSW)	0.89 lb wet MnO_2 (45% solids)	$0.02
HCl to regenerate adsorbent	1.33 lb 100% HCl	$0.32
NaOH for neutralization	0.91 lb 100% NaOH	$0.25
$BaCl_2$, NaCl for UIC disposal	4.6 lb	
H_2O in mixture for UIC disposal	17.2 lb	
Total UIC disposal	0.052 bbl	$0.57
Total Materials and Disposal		$2.35

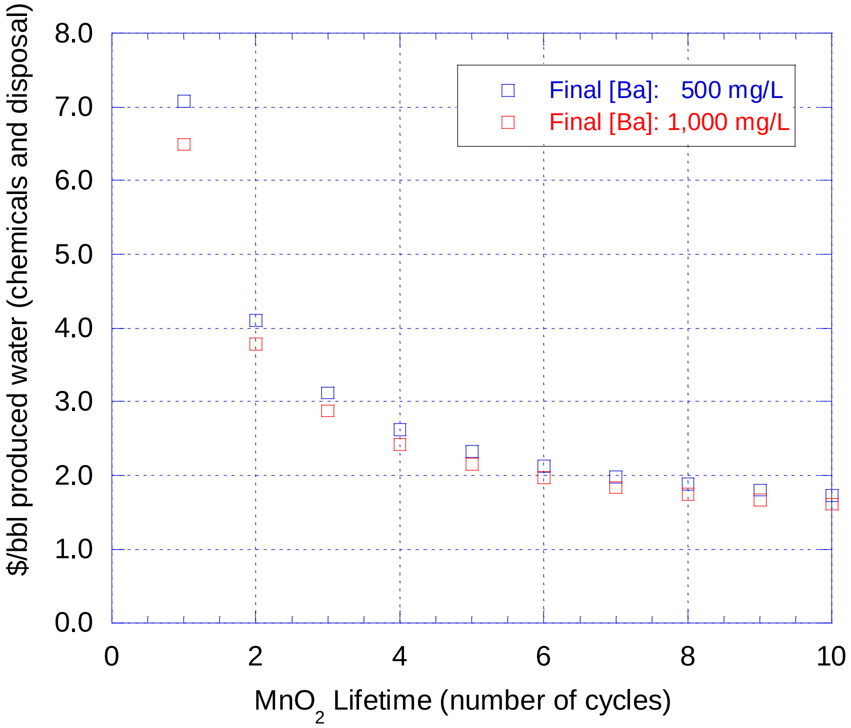

Figure 16. MnO_2 Adsorption-Regeneration Process Materials and Disposal Cost

V. Conclusions

For the Pennsylvania Marcellus in 2011, even with 95% produced water reuse, approximately 0.15-0.3MM gal/day of produced water must be disposed of by UIC. This volume will increase significantly as the supply of produced water exceeds the demand for water in subsequent hydrofracturing operations. The objective of this study was to identify cost-effective pretreatment technologies that enable thermal recovery of distilled water and a salable salt product from Type III produced waters that would otherwise need to be disposed of by UIC.

For the design case produced water composition, current technology enables water evaporation in either a mobile or stationary evaporator to recover about 56% of the produced water as distilled water and about 44% as a salt concentrate. The salt concentrate is disposed of by UIC. In 2011, GEWPT began testing its new mobile produced water evaporator that utilizes mechanical vapor recompression and treats about 60 gpm produced water.

To achieve 80-95% water recovery, it is necessary to generate a solid salt product in a thermal crystallizer. For use as road salt, the salt product must be greater than 95 wt% NaCl and must pass TCLP. Thus, the barium concentration in the TCLP extract must be less than 100 mg/L. In the absence of a specification, it is assumed that the ^{226}Ra activity in the salt product must be no greater than the level permitted for disposal as nonhazardous solid waste, which is 25 pCi/gm in Pennsylvania.

Based on a GEWPT pilot study of Marcellus produced water evaporation and salt crystallization, we developed a map of the produced water composition (barium concentration and ^{226}Ra activity) and the corresponding types of pretreatment required to obtain an acceptable salt product. We identified three types of produced waters. Type I produced waters contain barium concentrations less than $[Ba]_{max}$ (about 1,000-2,000 mg Ba/L) and are essentially unrestricted with respect to ^{226}Ra activity. Type I produced waters do not require barium or ^{226}Ra removal prior to NaCl crystallization.

Type II produced waters contain barium concentrations greater than $[Ba]_{max}$ and very low radium activities (<200-1,000 pCi ^{226}Ra/L; upper limit depends on the produced water barium concentration). These produced waters may be economically treated by sulfate precipitation prior to NaCl crystallization.

Type III produced waters have barium concentrations greater than $[Ba]_{max}$ and higher radium activities (>200-1,000 pCi ^{226}Ra/L; lower limit depends on the produced water barium concentration). Type III produced waters should not be treated by direct sulfate precipitation prior to NaCl crystallization because the resulting sulfate sludge ^{226}Ra activity would exceed state limits for disposal in RCRA-D landfills, and disposal as LLRW would be cost-prohibitive. This study focused on defining economical pretreatment processes for Type III produced waters.

The key to cost-effective barium and radium removal from Type III produced water is to generate a barium and radium concentrate that may be disposed of by UIC. We identified two such processes and conducted laboratory testing and cost analyses for each process.

The first pretreatment process is a modified lime-soda process that completely softens the produced water. Magnesium, calcium, and strontium are first precipitated to yield a solid sludge that can be disposed of as nonhazardous waste in a RCRA-D facility. This is followed by precipitation of barium and radium as carbonates. These carbonates are redissolved with HCl to yield a concentrate that can be disposed of by UIC. For the design case, about 0.05 bbl of concentrate for UIC disposal and about 25 lb. RCRA-D solid waste are generated per bbl raw produced water. For this case, the materials and disposal cost is estimated to be \$3.5/bbl produced water.

The second process utilizes high surface area MnO_2 as an adsorbent for barium and radium. The MnO_2 may be supported on mesoporous silica (as is the case for proprietary materials made by PNNL) or other supports. Alternatively, the MnO_2 may be in the form of activated MnO_2, which may be obtained commercially, or the MnO_2 may be prepared in-situ. MnO_2 is regenerated by treatment with dilute HCl. The regeneration process yields a concentrated solution of barium and radium, which may be disposed of by UIC. In laboratory studies, we demonstrated adsorption of barium and ^{226}Ra onto MnO_2. We also demonstrated regeneration of MnO_2 by HCl treatment to yield a reusable sorbent. For the design case produced water, we estimated the materials and disposal cost for a regenerable MnO_2 adsorbent to be in the range of \$1.7 to \$2.3 (adsorbent life 10 and 5 cycles, respectively) per bbl produced water. The volume of $BaCl_2$-$RaCl_2$ concentrate for disposal by UIC for the design case is estimated to be about 0.05 bbl per bbl produced water. Assuming that the spent MnO_2 adsorbent can be stripped of barium and radium sufficiently to be considered nonhazardous, the spent MnO_2 adsorbent may be disposed of in a RCRA-D landfill.

This modified lime-soda process is relatively simple and should be straightforward to scale up for commercial operation. This process results in essentially complete softening of the produced water, which increases water recovery and yields a higher grade salt product. This process appears to be in the best position for near-term implementation.

VI. Recommendations

Based on this investigation, the following recommendations are made.

> For the modified lime-soda process, a series of laboratory tests should be conducted to define both an effective agitation intensity (power per unit volume) and a range of reagent addition rates that give sufficient selectivity in the first carbonate precipitation process (Stage 1B in Figure 7).
>
> The MnO_2 adsorption process should be further developed in the laboratory to establish the feasibility of this process. Identification of an effective means of separation of MnO_2 particles from produced water and from regeneration streams is needed. Secondly, the regeneration purge stream to be disposed of must be concentrated (e.g. 20-30 wt% solids) for UIC, although the regeneration requires dilute HCl. The feasibility of using slightly acidic, concentrated $BaCl_2$-$RaCl_2$ solutions for desorption of $BaCl_2$ and $RaCl_2$ from MnO_2 must be established.
>
> Additional laboratory and pilot evaporation and crystallization studies should be conducted with produced waters that contain higher barium concentrations (e.g. 1,000, 2,000, and 5,000 mg Ba/L). This will enable a more robust estimate of the produced water barium concentration above which barium removal is needed.
>
> A ^{226}Ra specification for road deicing salt should be established.

VII. Acknowledgements

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[12] One picocurie (pCi) of radium is equal to 10^{-12} gm radium.

[13] The ratio of ^{226}Ra to ^{228}Ra will vary by location and it is not appropriate to assume that all waters within or between different formations will have a ratio of ^{226}Ra to ^{228}Ra in the range of 10/1.

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Appendix I. Selective Radium Removal from Produced Water

A. Literature Background

The National Drinking Water Clearinghouse has reported ion exchange, lime softening, and reverse osmosis as the best available technologies for removing radium from groundwater[1]. In addition, Deng[2] cites groundwater treatment for radium removal by low-pressure membrane filtration, manganese greensand filtration, MnO_2-impregnated resins, acid-washed sand filtration, and radium specific complexer (RSC) resins. Several chemical techniques for radium removal have been reported. These include sulfate treatment to coprecipitate radium and barium as $RaSO_4$ with $BaSO_4$, as discussed by Doener and Hoskins[3]. Bader[4] describes a pressurized sulfate precipitation method to remove radium, barium, and strontium from produced water. This method yields a solid sulfate product.

In an earlier study[5], we suggested the possibility of using a commercial RSC resin (e.g. DOWEX RSC) to selectively remove radium from produced water. Snoeyink et al[6] measured the radium capacity of RSC under a wide range of TDS levels. For example, at 2,500 mg/L TDS and with a feed radium concentration of 180 pCi/L, the measured radium capacity was 32,000 pCi/gm. However, at 40,000 mg/L TDS and a feed radium concentration of 250 pCi/L, the radium capacity was only 300 pCi/gm. In contrast, Mangelson et al[7] measured 3,500 pCi ^{226}Ra/gm for RSC resin for treating water softener regeneration brine, which had 40,600 mg/L TDS and 1,181 pCi ^{226}Ra/L. The barium level was not reported for the brines in the Mangelson study. These highly disparate results led us to conduct our own experimental study of the performance of RSC resin for radium removal from high-TDS brines. The results of our study are given below.

Several types of organic resins and inorganic materials have been used to remove radium from brines and ground waters. Since radium is a Group II metal, it is easily removed from dilute aqueous solutions such as well water with strong acid cation exchange resins. Wang[8] showed the effectiveness of 18 different inorganic ion exchangers for removing radium from simulated wastewater containing about 2100

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mg/L TDS, primarily $CaSO_4$, and 5037 pCi/L ^{226}Ra. Although most produced waters have significant levels of barium, the simulated wastewater in the Wang study did not contain barium. $BaSO_4$ as -100/+120 mesh granules (barite) and powdered $BaSO_4$ both showed distribution coefficients[9] for radium of the order of 3000-4000. This is equivalent to a radium capacity of 3000-4000 pCi/gm for a solution containing 1000 pCi/L radium. Wang describes the mechanism for radium removal from solution as a chemical exchange between the radium ions in solution and barium ions at the $BaSO_4$ crystal-solution interface. Based on this mechanism, it is expected that barium in the aqueous solution will decrease the effectiveness of a given material for radium removal.

Several metal oxides have been tested for removing radium from aqueous solutions. Nirdosh et al[10] measured equilibrium isotherms for aqueous ^{226}Ra solutions on oxides of Fe, Mn, Zr, and Ti. Among these oxides, only MnO_2 had significant adsorption capacity for ^{226}Ra.

Patel and Clifford[11] reported several adsorbents, for example hydrous manganese oxides, manganese-impregnated acrylic fibers, $BaSO_4$-impregnated alumina, untreated alumina, and iron and manganese precipitates for removing radium from groundwater. They found that water treatment by hydrous manganese oxide followed by diatomaceous earth filtration was both economical and effective for radium removal from radium-spiked Houston groundwater.

Moon et al[12] describe "MnO_2 Resin" from PG Research Foundation that adsorbs radium and barium from aqueous solutions. This material was prepared by a proprietary method utilizing reductive precipitation to generate MnO_2 on a macroporous resin substrate. This material has been utilized to concentrate radium from ground water and sea water at the laboratory scale. Moon found that with MnO_2 resin, the distribution coefficient for <u>both</u> radium and barium was 2.8×10^4 for adsorption from waters of a significant range of salinity (DI water, and waters containing 200, 3,500, and 35,000 mg/L TDS). Thus, MnO_2 showed no selectivity for radium over barium.

In addition, carbonaceous materials have been used to remove radium from saline solutions. For example, Rachkova et al[13] demonstrated adsorption of radium from

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[9] $K_d = \frac{(Ra\, activity\, on\, solid)/(gm\, solid)}{(Ra\, activity\, in\, solution)/(gm\, solution)}$

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[11] Patel, R. and Clifford, D., Radium Removal from Water by Manganese Dioxide Adsorption and Diatomaceous Earth Filtration, EPA Project Summary EPA/600/S2-91/063 (March, 1992).

[12] Moon, D.S., Burnett, W.C., Nour, S., Horwitz, E.P., and Bond A., Preconcentration of Radium Isotopes from Natural Waters using MnO2 Resin, Applied Radiation and Isotopes, 59 (2003) 255-262.

[13] Rachkova, N.G., Shuktomova, I.I., and Taskaev, A.I., Sorption of Uranium, Radium, and Thorium from Saline Solutions on Hydrolyzed Wood Lignin, Russian Journal of Applied Chemistry, 2006, Vol 79, No. 5, pp. 715-721.

saline solutions onto hydrolyzed wood lignin. Tsezos et al[14] investigated ^{226}Ra adsorption on granular activated carbon for uranium mine tailings.

3M Corporation supplies Empore™ disks to concentrate radium from water samples[15]. The active material is a crown ether covalently bound to inert substrate particles. This proprietary material has affinity for both radium and barium, and can be regenerated with 0.25M EDTA, which would generate a concentrate of radium and barium for UIC. This material is proprietary, and is designed for laboratory analytical procedures.

B. Adsorbent Screening

As shown above, most of the radium adsorption literature is focused on removing radium from groundwater or well water. To complement this information, we screened about 60 materials for their ability to remove radium from produced water. We utilized liquid scintillation counting (LSC) to measure the performance of each material. Both the analytical techniques for NORM measurement and laboratory safety for handling NORM-containing produced water have been discussed previously[16] and are included in Appendix IV. For this screening study, we utilized produced water from Well-4. This produced water sample has significantly lower TDS and barium levels than the other samples and may be considered a "best case scenario" for adsorbent screening. The screened materials included carbons, molecular sieves, clays such as montmorillonite, strong acid cation exchange resins, insoluble salts such as barium sulfate, and inorganic oxides, including MnO_2. For each test, 20 mL of Well-4 produced water and approximately 115 mg of an adsorbent were placed in a vessel and agitated overnight. The feed and each filtered liquid were subsequently measured for residual radioactivity by LSC. The reduction in counts per minute (vs. feed) is plotted for each adsorbent in Figure AI-1. This shows that among the materials screened, manganese oxide and barium sulfate are the most effective adsorbents for radium removal from field produced water that has modest TDS and a low barium level.

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[14] Tsezos, M and Keller, D.M., Adsorption of Radium-226 by Biological Origin Adsorbents, Biotechnology and Bioengineering, Vol. 25, No. 1, January 1983, pp. 201-215.

[15] Scarpitta, S.C., Evaluation of 3M Empore Rad Disks for Radium Determination in Water, 42nd Annual Conference of BioAssay, Analytical, and Environmental Radiochemistry, San Francisco, CA (1996).

[16] Silva, J.M., Matis, H., Kostedt, W.K. IV, and Watkins, V., Hydrofracturing Water Pretreatment for Water and Salt Recovery, International Water Conference Paper IWC-11-7, November, 2011, Orlando, FL.

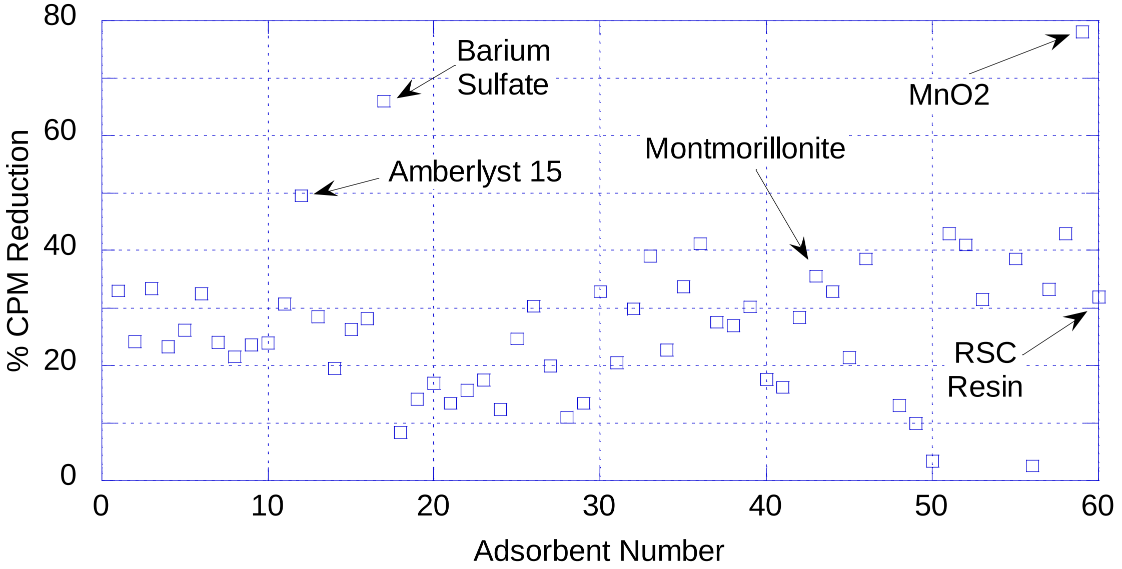

Figure AI-1. Radium Removal Performance for Screened Adsorbents

C. DOWEX RSC Resin for Radium Removal from Produced Water

We tested DOWEX RSC resin for selectively removing radium from produced water. Figure AI-2 shows a scanning electron micrograph of a resin bead that was fractured by immersion in liquid nitrogen followed by a light tap with a hammer. The white spots represent $BaSO_4$ microcrystallites. The characteristic dimension of the microcrystallites is typically 20-40 nm[17].

These bound $BaSO_4$ crystallites ion exchange with radium as shown in equation (1).

$$RaCl_{2(aq)} + BaSO_{4(resin)} \rightarrow RaSO_{4(resin)} + BaCl_{2(aq)} \tag{1}$$

Attempts have been made to regenerate RSC resin[18]. However, these attempts have been unsuccessful, primarily because $RaSO_4$ is so stable. Therefore, it is assumed that RSC resin is a single-use ion exchange resin for radium removal. Spent RSC resin is typically disposed of as LLRW. RSC resin is often utilized to remove radium from brine that is used to regenerate water softening ion exchange resins in municipal water systems. In a demonstration study[19], hardness (Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}) and radium were removed from drinking water using a conventional gelular sulfonic acid ion exchange resin (sodium form). The softening ion exchange resin was regenerated with NaCl brine (average 40,600 mg/L TDS) to remove hardness and radium. The regeneration brine

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[17] Silva, J.M., Matis, H., Tinto, J.V., NORM Removal from Frac Water in a Central Treatment Facility, International Water Conference paper IWC-10-65, San Antonio, TX, October, 2010.

[18] Arnold, W.D., and Crouse, D.J., Radium Removal from Uranium Mill Effluents with Inorganic Ion Exchangers, I&EC Process Design and Development, Vol. 4, No. 3, July, 1965.

[19] Mangelson, K.A. and Lauch, R.P., Removing and Disposing of Radium from Well Water, Journal of the American Water Works Association, **82** (6), 72-76 (1990).

leaving the ion exchange resin contained an average of 1180 pCi radium/liter (the barium level in this stream was not reported). Prior to disposal, this regeneration brine was treated with RSC resin. The RSC resin removed an average of 99.2% of the radium from the softener regeneration brine. After one year of operation, the resin loading was 3,000 pCi/cc resin.

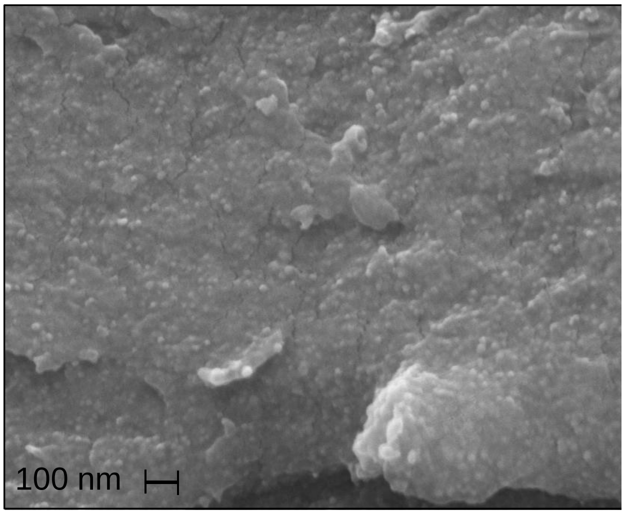

Figure AI-2. SEM of DOWEX RSC Resin (50K magnification)

1. DOWEX RSC Resin Economics

The cost of DOWEX RSC resin is approximately \$500/ft^3. Waste containing up to 10,000 pCi/gm can be disposed of as LLRW, which costs about \$200/ft^3 for disposal. Figure AI-3 shows the cost of both resin and LLRW disposal for two levels of feed ^{226}Ra activity as functions of the adsorbent capacity[16]. This figure shows that by loading a resin at 10,000 pCi ^{226}Ra/gm, the resin plus disposal cost adds \$1.25-\$2.50/bbl to the cost of recovering water and salt from produced water, depending on the raw produced water ^{226}Ra activity. Thus, for a non-regenerable material such as RSC resin, the target loading level is 10,000 pCi ^{226}Ra/gm resin.

2. RSC Resin Performance

We selected DOWEX RSC resin for further testing because it showed promising results in the screening tests and it is commercially available. Much Marcellus produced water has barium and TDS levels higher than those of Well-4. Therefore, we conducted two series of batch equilibrium capacity tests with produced waters that had been spiked with various barium levels. The details of both the capacity measurements and the equations for estimating ^{226}Ra capacity from LSC measurements are given in Appendix IV. Produced waters from Well-4 (low TDS) and Well-7 (high TDS) were each spiked with barium to measure the effects of TDS and barium concentration on the radium capacity of DOWEX RSC resin. Barium was added to the produced water as $BaCl_2$, which was obtained from Sigma-Aldrich®.

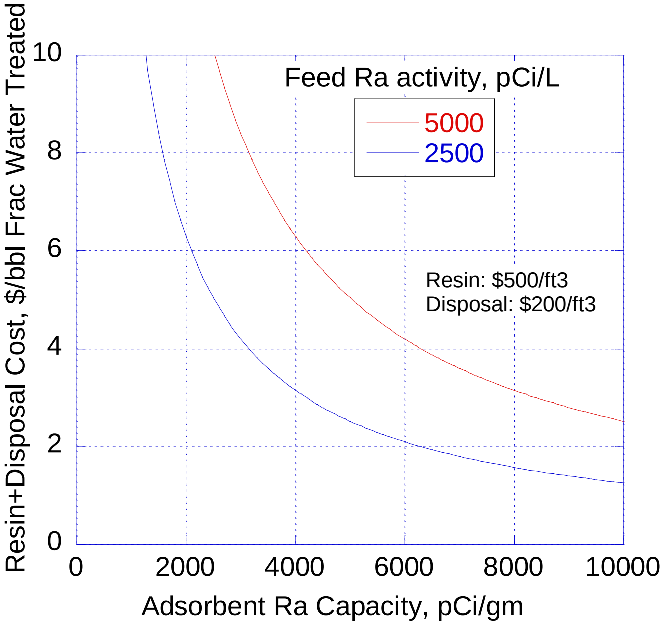

Figure AI-3. Resin and Disposal Cost Sensitivity to Adsorbent Capacity and Produced Water Feed ^{226}Ra Activity

Figure AI-4 shows the effects of both TDS and Ba concentration on the apparent capacity of DOWEX RSC resin for ^{226}Ra. The capacity was calculated based on the measured reduction in LSC counts per minute above background due to resin treatment and the measured feed ^{226}Ra levels. This figure shows that the resin ^{226}Ra capacity with unspiked Well-4 brine is comparable to that reported by Snoeyink[6]. This measured ^{226}Ra capacity is far too low to be commercially practical, even for Well-4 produced water. The radium capacity decreases significantly with increasing barium levels. For the higher TDS brine of Well-7, the capacity is virtually negligible at all barium levels. These results led us to seek alternate sorbents, as well as alternate processes for removing radium from produced water.

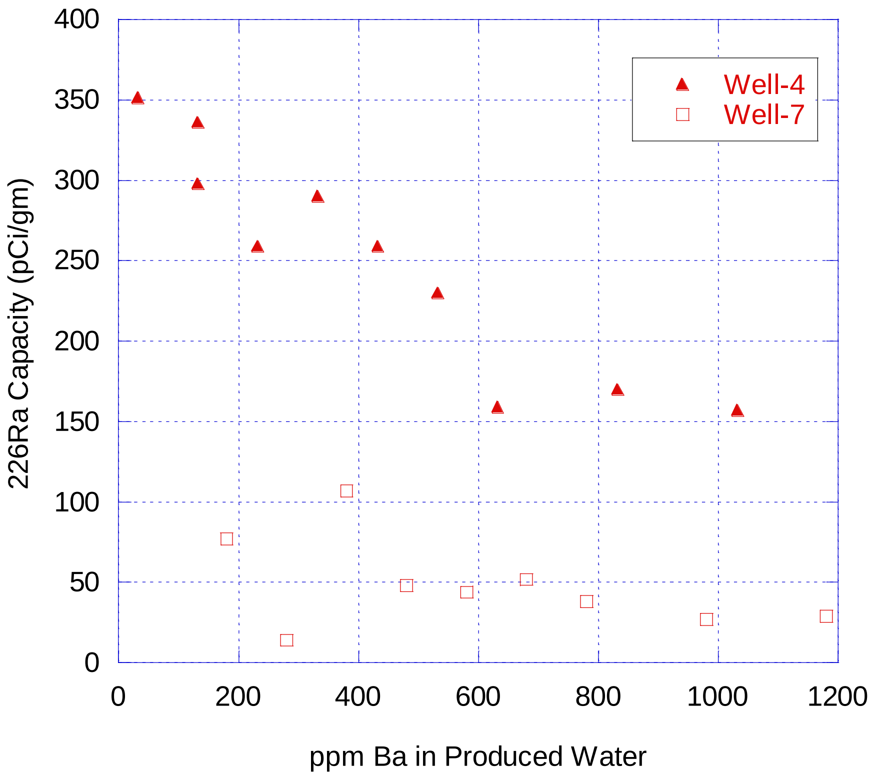

Figure AI-4. Effects of TDS and Barium Concentration on RSC ^{226}Ra Capacity

Appendix II. Produced Water Softening by Ion Exchange

A. Background

In the chlor-alkali industry, ion exchange (IEX) is used extensively for secondary sodium chloride brine purification prior to electrolysis in membrane electrolyzers. Chelating IEX resins such as aminomethylphosphonic acid (AMP)- and iminodiacetic acid (IDA)-functionalized polystyrene are used to soften concentrated NaCl brine solutions. Figure AII-1 shows a possible structure for the complex between a divalent cation and AMP-functionalized polystyrene[1]. The ion exchange capacity of commercially available AMP resins is typically 14 gm Ca per liter resin under chlor-alkali purification conditions (60°C, 300 gm/liter NaCl, 15 mg/L Ca, pH 9.5, 10 bed volumes/hr)[2]. Prior to ion exchange resin treatment, the brine must be treated to remove suspended solids to below 10 microns[3]. In this application, the feed hardness level (calcium plus magnesium) is typically 1-10 mg/L; the treated product hardness level is below 20 µg/L.

Produced water for use in once-through steam generators (OTSG) has been demineralized using ion exchange technology[4]. For the OTSG application, the produced water TDS was in the range of 4,000-7,100 mg/L and the hardness level was 447 mg/L as $CaCO_3$. Both the TDS and hardness are about a factor of 20 lower than the corresponding frac water values.

Produced water from coal bed methane (CBM) extraction has also been purified using ion exchange technology. Marathon has awarded Eco-Tec a service contract to utilize a Recoflo system to demineralize produced water from CBM in the Powder River Basin in Wyoming[5]. The system is designed to treat 1.5 MGD (36,000 bpd) produced water. The TDS range of the produced water to be treated was not specified, but a DOE survey of the Powder River Basin CBM produced waters utilized 1,500 mg/L TDS as a working value to compare the cost of Powder River Basin CBM produced water demineralization by ion exchange and reverse osmosis[6]. The TDS level for CBM demineralization is two orders of magnitude lower than the design case frac water TDS and an order of magnitude lower than the design case hardness level.

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[1] Kiefer, R. and Hoell, W., Sorption of Heavy Metals onto Selective Ion-Exchange Resins with Aminophosphonate Functional Groups, *Ind. Eng. Chem. Res.* 2001, *40,* 4570-4576.

[2] Wolff, J.J. and Anderson, R.E., Ion-Exchange of Feed Brine for Chlor-Alkali Electrolysis Cells: The Role of Duolite ES-467, Presentation at AIChE Meeting, Orlando, Fl, Spring, 1982.

[3] Cocurek, D. and Woodside, G., Waste Treatment, Hazardous Waste, Kirk-Othmer Encyclopedia of Chemical Technology, p. 8, (Dec. 4, 2000).

[4] Krause, L., Sheedy, M., and Jones, K., Produced Water Recovery at Seneca Resources Using Short Bed Ion Exchange, International Water Conference Paper IWC-10-21, San Antonio, TX, 2010.

[5] PRNEWSWIRE, May 8, 2008. http://www.prnewswire.com/news-releases/eco-tec-awarded-cbng-produced-water-treatment-system-contract-by-marathon-oil-corporation-57216457.html

6 Bank, G. and Kuuskraa, V., The Economics of Powder River Basin Coalbed Methane Development, Report prepared for DOE, 2008.

A continuous IEX system, the Higgins Loop™, has been utilized commercially since 1955 for a variety of water softening and demineralization applications. Based on countercurrent contact between IEX resin and the feedwater, this process generates lower regeneration and rinse volumes than traditional co-current flow systems[7,8]. No reference was found in which the Higgins Loop was applied to softening brines comparable to the design case.

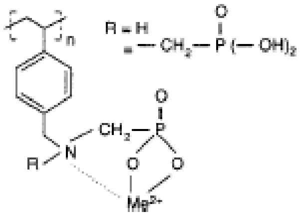

Figure AII-1. AMP-Functionalized Polystyrene Resin

Chelating ion exchange resins (also referred to as weak acid cation exchange resins, or WAC) are regenerated by a multiple step process. First, strong acid (2-4 M or 5-15 wt% HCl) is used to displace hardness from the resin with protons. Following a deionized (DI) water rinse, 2-4 M NaOH (5-15 wt%) is used to displace protons with sodium ions. The resin is rinsed again with DI water and placed back into service. The regeneration solutions, comprising an acidic solution of concentrated alkaline earth metal chlorides ($MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$), and a basic solution of NaCl are typically mixed, neutralized, and disposed of as wastewater.

The design case produced water contains the equivalent of 13,772 mg/liter of Ca^{++} cations, which equals 0.687 gm-equivalents of hardness per liter of frac water (109.3 gm-equivalents per bbl frac water). The resin capacity for removing hardness from frac water is assumed to be 14 gm Ca^{++} (0.70 gm-equivalents of hardness) per liter resin[9]. Based on this assumed capacity, *0.98 volumes of IEX resin are required per volume of frac water to soften frac water* for the design case. Thus, the ion exchange resin bed will become exhausted after the first bed volume of frac water passes through. Chemical costs and waste volumes for regeneration will therefore dominate the cost of using ion exchange to soften frac water. The calculations given here represent a best case scenario; finite mass-transfer zones for ion exchange unit operations will cause actual

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[7] Higgins, I.R., Treating Brackish Water for High Pressure Boiler Makeup For Thermal Flooding by Continuous Ion Exchange: A Case History At Coronado Oil Company, Fall Meeting of the Society of Petroleum Engineers of AIME, 1-4 October 1967, New Orleans, Louisiana, 1967.

[8] Higgins, I.R., Continuous Ion Exchange Equipment, Industrial and Engineering Chemistry, vol. 53, No. 8, August, 1961.

[9] McKetta, J.J., Encyclopedia of Chemical Processing and Design: vol 51, Slurry Systems, Instrumentation to Solid-Liquid Separation, 1995, CRC Press.

regeneration chemical usage and waste stream generation to be higher than those reported here.

B. Acid Treatment

The first step in regeneration of a chelating ion exchange resin is an HCl treatment to strip divalent cations from the resin as their chlorides, as shown in equation (1).

$$Resin_2\text{-}Ca + 2HCl \rightarrow 2Resin\text{-}H + CaCl_2 \tag{1}$$

Equation (2) shows the HCl usage for regeneration for this case.

$$\left(\frac{0.687\ mole\ HCl}{liter\ \ frac\ water}\right)\left(\frac{169\ liter}{bbl}\right)\left(\frac{36.5\ gm\ HCl}{mole\ HCl}\right)\left(\frac{lb\ HCl}{454\ gm\ HCl}\right) = \frac{8.78\ lb\ Regen\ HCl\ (dry)}{bbl\ \ frac\ water} \tag{2}$$

Equation (3) shows the volume of concentrated (35.2 wt%) HCl required per bbl frac water.

$$\left(\frac{8.78\ lb\ dry HCl}{bbl\ \ frac\ water}\right)\left(\frac{lb\ HCl\ soln}{0.352\ lb\ dry\ HCl}\right)\left(\frac{gallon\ HCl\ soln}{1.175 \times 8.33\ lb\ HCl\ soln}\right) = \frac{2.54\ gallon\ HCl\ soln}{bbl\ \ frac\ water} \tag{3}$$

The cost of HCl (2009) is about \$525/metric ton for 35.2 wt% HCl (100% basis)[10]. Assuming complete reaction of HCl for regeneration[11], the cost of HCl for IEX regeneration is shown in equation (4). For IEX regeneration, a 5-15 wt% HCl stream would be recirculated between a tank and the IEX resin bed. The HCl concentration is maintained in the tank by addition of concentrated (e.g. 35.2 wt%) HCl to the HCl regeneration tank.

$$\left(\frac{8.78\ lb\ dry\ HCl}{bbl\ \ frac\ water}\right)\left(\frac{\$525}{2200\ lb\ dry\ HCl}\right) = \frac{\$2.09\ Regen\ HCl}{bbl\ \ frac\ water} \tag{4}$$

The HCl treatment generates an acidic chloride solution of the hardness cations. Based on a target final $CaCl_2$ concentration of 30 wt% (as $CaCl_2$), the initial HCl concentration needs to be 22.2 wt% HCl. The amount of DI water required to make up this solution from 35.2 wt% HCl feed is calculated below.

The amount of $CaCl_2$ generated per barrel frac water is given by equation (5).

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[10] SRI Consulting, Chemical Economics Handbook (HCl: 2009; NaOH: 2008).

[11] i.e. 100% of HCl added to system is used to displace hardness from IEX resin.

$$\left(\frac{109.3\,gm\text{-}equivalent}{bbl\ \ frac\,water}\right)\left(\frac{111\,gm\,CaCl_2}{2\,gm\text{-}equiv}\right)\left(\frac{lb}{454\,gm}\right)=\frac{13.37\,lb\,CaCl_2}{bbl\ \ frac\,water} \tag{5}$$

For a 30 wt% solution of $CaCl_2$, the amount of H_2O in the regeneration solution per barrel frac water is given by equation (6).

$$\left(\frac{13.37\,lb\,CaCl_2}{bbl\ \ frac\,water}\right)\left(\frac{1\text{-}0.3\,lb\,H_2O}{0.3\,lb\,CaCl_2}\right)=\frac{31.19\,lb\,H_2O\ in\ regen\ soln}{bbl\ \ frac\,water} \tag{6}$$

The amount of water in the concentrated (35.2 wt%) HCl used for regeneration (per bbl frac water treated) is calculated in equation (7).

$$\left(\frac{2.54\ gal\ conc\ HCl}{bbl\ \ frac\,water}\right)\left(\frac{8.33*1.175\ lb\ conc\ HCl}{gal\ conc\ HCl}\right)\left(\frac{1\text{-}0.352\ lb\ H_2O}{lb\ conc\ HCl\ soln}\right)=\frac{16.1\,lb\,H_2O}{bbl\ \ frac\,water} \tag{7}$$

The amount of DI water (or possibly filtered frac water or softened frac water) needed per barrel frac water is given by equation (8).

$$\left(\frac{31.19\text{-}16.14\ lb\,H_2O}{bbl\ \ frac\,water}\right)\left(\frac{1\ gal\ H_2O}{8.33\ lb\ H_2O}\right)=\frac{1.81\,gal\ H_2O\ added}{bbl\ \ frac\,water} \tag{8}$$

The $CaCl_2$ (equivalent) concentrate will be disposed of by UIC. It is assumed that this concentrate is generated in North-Central Pennsylvania and transported and disposed of in Ohio, at a cost of \$11/bbl (transportation plus UIC cost). The volume of concentrate from the HCl regeneration step and the cost of disposal are calculated in equations (9) and (10), respectively.

$$\frac{\left(\frac{13.37\,lb\,CaCl_2}{bbl\ \ frac\,water}\right)\left(\frac{1\ lb\ CaCl_2\ solution}{0.3\ lb\ CaCl_2}\right)}{\left(\frac{8.33\ lb\ H_2O}{gallon}\right)\left(1.2816\ spgr\ CaCl_2\ solution\right)}=\frac{4.18\ gal\ CaCl_2\ solution}{bbl\ \ frac\ water} \tag{9}$$

$$\left(\frac{4.18\,gal\,CaCl_2\ soln}{bbl\ \ frac\,water}\right)\left(\frac{bbl\ soln}{42\ gal\,soln}\right)\left(\frac{\$11\ disposal\ cost}{bbl\ soln}\right)=\frac{\$1.09\ disposal\ cost}{bbl\ \ frac\,water} \tag{10}$$

C. Rinse

After the HCl treatment, the resin must be rinsed with at least one bed volume of a neutral water stream. The purpose of the rinse step is to displace acid solution (which contains divalent cations such as Mg^{++}, from the resin so that they do not precipitate during the subsequent NaOH treatment. In the chlor-alkali industry, DI water is used for this rinse. In this application, a softened brine stream could be used. The volume of rinse is calculated in equation (11).

$$\left(\frac{0.687\ equiv\ Ca^{++}}{liter\ \ frac\ water}\right)\left(\frac{liter\ IEX\ resin}{0.70\ equiv\ Ca^{++}}\right)\left(\frac{1\ liter\ rinse}{liter\ IEX\ resin}\right)\left(\frac{\frac{1\ bbl\ rinse}{159\ liter\ rinse}}{\frac{1\ bbl\ \ frac\ water}{159\ liter\ \ frac\ water}}\right)=\frac{0.98\ bbl\ rinse}{bbl\ \ frac\ water} \quad (11)$$

For the design case, the rinse stream is essentially the same volume as the frac water being treated. Since the purpose of the rinse stream is to remove residual divalent cations from the resin, the rinse source stream must be substantially free of divalent cations. Therefore, to conduct this rinse step, a clean source water stream is required. Further, this rinse stream cannot be discharged to surface water because it may have excess TDS and barium levels. The cost of disposal of this rinse stream by UIC is comparable to the cost of disposal of the original frac water.

D. NaOH Treatment

The second step in regeneration of chelating ion exchange resin is to treat the resin with NaOH, as shown in equation (12).

$$Resin\text{-}H+NaOH \rightarrow Resin\text{-}Na+H_2O \quad (12)$$

The NaOH usage is calculated in equation (13).

$$\left(\frac{0.687\ mole\ NaOH}{liter\ \ frac\ water}\right)\left(\frac{159\ liter}{bbl}\right)\left(\frac{40\ gm\ NaOH}{mole\ NaOH}\right)\left(\frac{lb\ NaOH}{454\ gm\ NaOH}\right)=\frac{9.63\ lb NaOH}{bbl\ \ frac\ water} \quad (13)$$

For IEX regeneration, a 5-15 wt% NaOH stream is recirculated between a tank and the IEX resin bed. The NaOH concentration in the tank is maintained by adding concentrated (e.g. 50 wt%) NaOH to the tank. Equation (14) shows the volume of makeup 50 wt% NaOH required per bbl frac water.

$$\left(\frac{9.63\ lb\ dry\ NaOH}{bbl\ \ frac\ water}\right)\left(\frac{lb\ NaOH\ \ soln}{0.50\ lb\ dry\ NaOH}\right)\left(\frac{gallon\ NaOH\ \ soln}{1.52\times 8.33\ lb\ NaOH soln}\right)=\frac{1.52\ gal NaOH soln}{bbl\ \ frac\ water} \quad (14)$$

The cost of NaOH is highly variable over time and geography. The most recent price reported by SRI (2008) is \$610/dry metric ton for 50 wt% NaOH[10]. Assuming complete reaction of NaOH for IEX regeneration, the cost of NaOH for IEX regeneration is shown in equation (15).

$$\left(\frac{9.63\ lb\ dry\ NaOH}{bbl\ \ frac\ water}\right)\left(\frac{\$610}{2200\ lb\ dry\ NaOH}\right)=\frac{\$2.67\ Regen\ NaOH}{bbl\ \ frac\ water} \quad (15)$$

The NaOH regeneration brine stream is typically combined with the spent HCl regeneration stream and disposed of by UIC. The NaOH regeneration brine stream comprises water from the original 50 wt% solution plus the water resulting from equation (12), as well as residual NaOH. Conceivable, some or all of this water may be used to dilute the $CaCl_2$ stream generated by HCl treatment (equation (8)).

$$\left(\frac{9.63\ lb\ NaOH}{bbl\ \ frac\ water}\right)\left(\frac{0.5\ lb\ H_2O}{0.5\ lb\ NaOH}+\frac{18\ lb\ H_2O}{40\ lb\ NaOH}\right)=\frac{13.96\ lb\ regen\ brine}{bbl\ \ frac\ water} \qquad (16)$$

The cost for disposal of this brine stream is calculated in equation (17).

$$\left(\frac{13.96\ lb\ brine}{bbl\ \ frac\ water}\right)\left(\frac{gal}{8.33\ lb}\right)\left(\frac{bbl}{42\ gal}\right)\left(\frac{\$11\ disposal}{bbl\ brine}\right)=\frac{\$0.44\ disposal}{bbl\ \ frac\ water} \qquad (17)$$

E. Rinse

After NaOH treatment, the resin bed must be rinsed with at least one bed volume of deionized or softened water rinse. This is to avoid precipitation of species such as $Mg(OH)_2$ on the resin bed after placing the ion exchange system back into service after NaOH treatment. Again, the volume of this rinse will be comparable to the volume of frac water being treated.

F. Summary

Table AII-1 shows the calculated chemical and disposal costs for both the acid and base treatment steps. The cost of disposing the rinse water, while not included in this table, would be approximately double the cost of disposing all of the frac water by UIC. For brines with such high hardness levels as the design case, the use of chelating ion exchange resin is neither economical nor practical.

Table AII-1. Regeneration Chemical Usages and Costs

Chemical	Usage: lb 100% chemical/ bbl frac water	Usage: gal solution/ bbl frac water	Cost: $/dry metric ton	Cost: $/bbl frac water
HCl	8.78	2.54	$525	$2.09
HCl brine disposal				$1.09
NaOH	9.63	1.52	$610	$2.67
NaOH brine disposal				$0.44
Total				$6.29

Appendix III. Produced Water Softening by Nanofiltration

A. Background

Nanofiltration (NF), shown schematically in Figure AIII-1, was originally developed as a method to achieve higher water fluxes at lower differential pressures and therefore lower energy costs than those associated with reverse osmosis (RO) membranes. NF provides an alternative to RO for applications where an extremely high-quality permeate product is not required. NF rejects substances by two mechanisms: neutral species are rejected by size (molecules larger than 200-300 gm/mole are rejected) and inorganic ions are rejected due to electrostatic interactions with the membrane[1]. Although the size range for rejection associated with NF overlaps those of ultrafiltration and reverse osmosis, the defining feature of NF is high rejection of *multivalent* ions combined with relatively low rejection of *monovalent* ions. This property makes NF attractive for water softening applications where desalination is not a key goal and it is desirable to achieve high removal of divalent ions such as calcium and magnesium while retaining high water flux.

Because the permeability of monovalent ions through NF membranes is so much greater than with RO, the feed pressure to an NF system is much lower than the feed pressure to an RO system. The maximum operating pressures of NF membranes also tend to be lower than those of RO.

The use of NF membranes in drinking water applications has been reviewed by Thorsen et al[2]. NF competes with traditional softening processes such as ion exchange and lime softening, especially at larger facilities. The product quality is better than that of lime softening due to the removal of color and turbidity, while process flexibility, lower footprint, and zero sludge production also make NF attractive. Also, recent advances in reducing operating pressure requirements continue to improve the cost-effectiveness of NF[3]. Potential issues include treatment and/or disposal requirements for the concentrate stream, as well as membrane fouling and subsequent cleaning requirements. In addition, NF membranes are sensitive to both suspended solids and dissolved oxidizers such as chlorine. Membrane fouling may occur both by scaling of inorganic compounds such as $CaCO_3$ or $CaSO_4$ as well as by deposition of organic compounds or biofouling.

Unlike ion exchange and lime softening, NF requires no regeneration chemicals and only minimal additives (e.g. antiscalants). The concentrate stream from NF processes is brine

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[1] Linde, K., Jonsson, A., Nanofiltration of Salt Solutions and Landfill Leachate, Desalination, 103 (1995) 223-232.

[2] Thorsen, T. and Fl∅gstad, H., Nanofiltration in Drinking Water Treatment: Literature Review, Techneau, D5.3.4B, December, 2006.

[3] Li, N.N. et al., Advanced Membrane Technology and Applications, John Wiley & Sons, 2008.

with a high concentration of multivalent species; this concentrate requires disposal by UIC.

In a lab study with 1M brines (58,000 mg/L NaCl) comprising primarily monovalent anions, the retention of multivalent cations was higher than 70%, while the retention of sodium ions was less than 10%. The flux was 50 L/m^2-hr for a transmembrane pressure of only 435 psi[4]. The permeate recovery was not reported in this study.

NF has been used to selectively remove multivalent ions from aqueous feed streams in water softening applications[5]. NF has been used, for example, to soften feedwater to seawater multistage flash units[6] and to remove divalent cations from concentrated landfill leachate solutions[1].

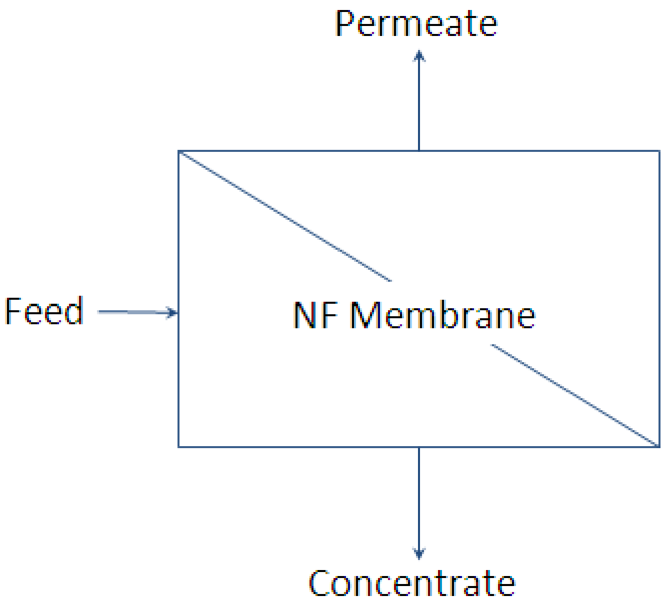

Figure AIII-1. Schematic Diagram of NF Separation Process

B. WINFLOWS Calculations

We utilized WINFLOWS 3.0 from GE Water and Process Technologies to simulate a NF application[7]. The NF membrane tested was GEWPT membrane HR8040. The maximum allowable pressure was set to 600 psi. The objective of these calculations was to estimate the maximum permeate water recovery. Flux rates in each element were allowed to be outside of design guidelines.

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[4] Linde, K., Jonsson, A., op. cit.

[5] Nanda, D., et. al., op. cit.

[6] Awerbuch, L., ''Nanofiltration: the Great Potential in Reducing Cost of Desalination'' Proceedings of IDA World Congress Singapore, September 2005.

[7] WINFLOWS 3.0 is available for download from: http://www.gewater.com/winflows.jsp.

1. Case I: Design Case Produced Water Softening

The design case produced water was fed at 50 gpm to a two-stage configuration. Four NF modules in parallel comprise the first stage, and 8 modules in parallel comprise the second stage. The feed pressure to the first stage was 514.9 psia, and the feed to the second stage was 599.6 psia.

The selectivity for divalent cation rejection was significant (e.g. the Mg^{++} concentration in the permeate was a factor of 10.8 lower than in the feed). There was essentially no rejection of monovalent cations. The calculated water recovery is 30.0 percent. Table AIII-1 shows the results for this simulation.

Table AIII-1. NF Simulation Results for Design Case Produced Water
(units mg/L except as indicated)

Component	Feed	Concentrate	Permeate
TDS	132,460	149,886	96,986
Na^+	35,000	34,948	35,085
Mg^{++}	800	1,157	74.1
Ca^{++}	9,500	13,305	1,767
Ba^{++}	6,200	8,683	1,152
Sr^{++}	2,500	3,500	467
Fe	50	70.0	9.37
Mn	3	4.20	0.56
Cl^-	58,008	88,218	58,431
pH	7.00	6.99	7.03
Rate (gpm)	50.00	35.01	14.99

2. Case II: Well-5 Produced Water Softening

The process configuration for Case I was also used in this case. Both the hardness and TDS for Well-5 produced water are higher than the design case. According to the simulation, the maximum water recovery for this feed was 15.2%. For water recoveries above 15.2%, the required feed pressure exceeds the 600 psia limitation on the membrane modules. Table AIII-2 shows the results for this simulation. As in Case I, there is essentially no rejection of monovalent cations. The Mg^{++} concentration in the permeate was a factor of 7 lower than the corresponding concentration in the feed.

Table AIII-2. NF Simulation Results for Well-5 Produced Water
(units mg/L except as indicated)

Component	Feed	Concentrate	Permeate
TDS	149,149	156,545	11,972
Na^+	39,000	38,927	39,339
Mg^{++}	1,000	1,176	141
Ca^{++}	13,000	14,944	3,502
Ba^{++}	3,500	4,024	942
Sr^{++}	2,600	2,989	701
Fe	32.0	36.78	8.65
Mn	2.70	3.10	0.73
Cl^-	90,014	94,446	68,337
pH	5.90	5.85	6.13
Rate (gpm)	50.00	41.50	7.61

3. Operating Costs

Table AIII-3 shows the cost of electricity to operate a NF system for the two produced waters considered here. The electricity cost is assumed to be $0.10/kWh.

Table AIII-3. Key NF Softening Operating Costs

Produced Water	Electricity Usage (kWh/bbl)	Electricity Cost ($/bbl)	Maximum Permeate Recovery, %	Concentrate Transportation and Disposal Cost, $/bbl feed
Design Case	0.19	0.02	30	7.70
Well-5	0.19	0.02	15	9.35

The dominant cost for produced water softening by NF arises from the low water recoveries predicted by the simulations. The NF concentrate stream would need to be disposed of by deep-well injection (UIC). The estimated cost for concentrate transportation from central Pennsylvania to Ohio and disposal by UIC is $11/bbl. This cost and the large amount of transportation required makes the use of NF for produced water softening impractical.

Appendix IV. Modified Lime-Soda Process Analysis and Experimental Results

A. Equilibrium Material Balance Calculations with Aspen Plus/OLI

We utilized Aspen Plus with an electrolyte property package from OLI Systems for all material balance calculations described in this appendix. Figure AIV-1 shows the process flow diagram for these calculations. Produced water is first treated with $Ca(OH)_2$ to precipitate magnesium as $Mg(OH)_2$. The lime slurry (LIM-SLRY) is filtered in FILTER-1 and the filtrate is sent to an optional NaOH precipitation step. No NaOH was added in any of the simulations reported here. Thus, the stream labeled OVERFLOW is the same as the stream labeled OH-FLTRT. Sodium carbonate is added in the block labeled CO3-PPT to generate a carbonate slurry. This slurry is filtered in the block labeled CO3-FLTR to yield the softened produced water product, CO3FLTRT and the precipitate, CO3-PPT. For all the disposal calculations, it is assumed that the precipitates are 45 wt% solids (balance water).

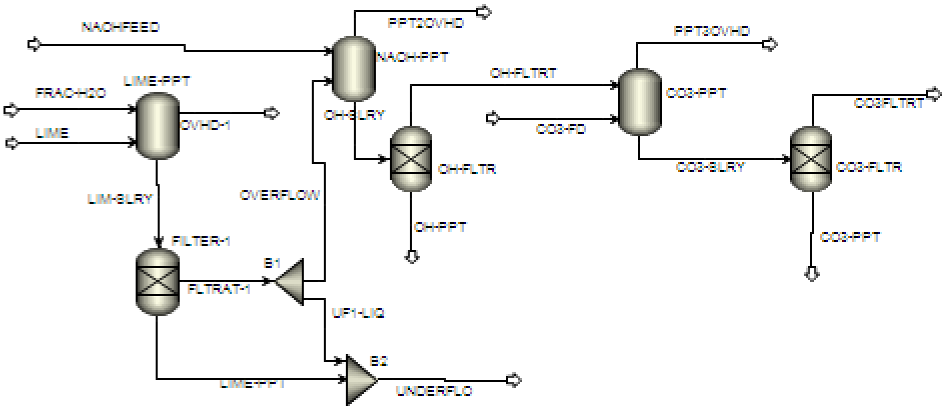

Figure AIV-1. Process Flow Diagram for Aspen Plus/OLI Simulations

Table AIV-1 shows the flow rates of each feed component used in these calculations. The total flow rate was about 1 MGD (million gallons/day) for each produced water simulation. We conducted sensitivity studies in the lime precipitation step to define the amount of lime required to precipitate essentially all of the magnesium in the raw produced water. We fixed the lime usage at the lowest multiple of 25 lb/hr $Ca(OH)_2$ for which essentially all the magnesium precipitated as $Mg(OH)_2$. For all cases, addition of 1.005-1.03 moles of $Ca(OH)_2$ per mole magnesium in the feed produced water was sufficient to precipitate essentially all of the magnesium in the feed produced water.

With the $Ca(OH)_2$ addition rate fixed, we conducted sensitivity studies in which we varied the rate of Na_2CO_3 addition to the lime-treated produced water. Figure AIV-2 through Figure AIV-9 show the calculated equilibrium composition of the produced water as a function of the amount of Na_2CO_3 added. For each case, as Na_2CO_3 is added, essentially all of the calcium and strontium precipitate as carbonates prior to any barium (and therefore radium) carbonate precipitation. This selectivity is the basis for the modified lime-soda process.

Table AIV-1. Produced water Component Feed Rates for Aspen Plus/OLI Simulations (all units lb/hr except where noted)

	Well-1	Well-2	Well-3	Well-4	Well-5	Well-6	Well-7	Design
H2O	347622	327658	312522	358011	329934	339184	338543	335737
NaCl	23422	33764	45784	16970	34471	28549	29963	30935
MgCl2	627	1144	1757	776	1362	1090	1594	1090
CaCl2	5353	9898	12632	5161	12517	8377	10475	9147
SrCl2	1277	2309	2881	811	1636	1472	1101	1573
BaCl2	3469	6959	6116	17	1845	3058	78	3269
FeCl2	21	58	97	43	25	59	37	39
MnCl2	1	2	3	1	2	3	1	2
Total	381792	381792	381792	381792	381792	381792	381792	381792
MGD[a]	1.03	1.00	0.97	1.05	1.00	1.02	1.02	1.01

[a] MGD: million gallons/day

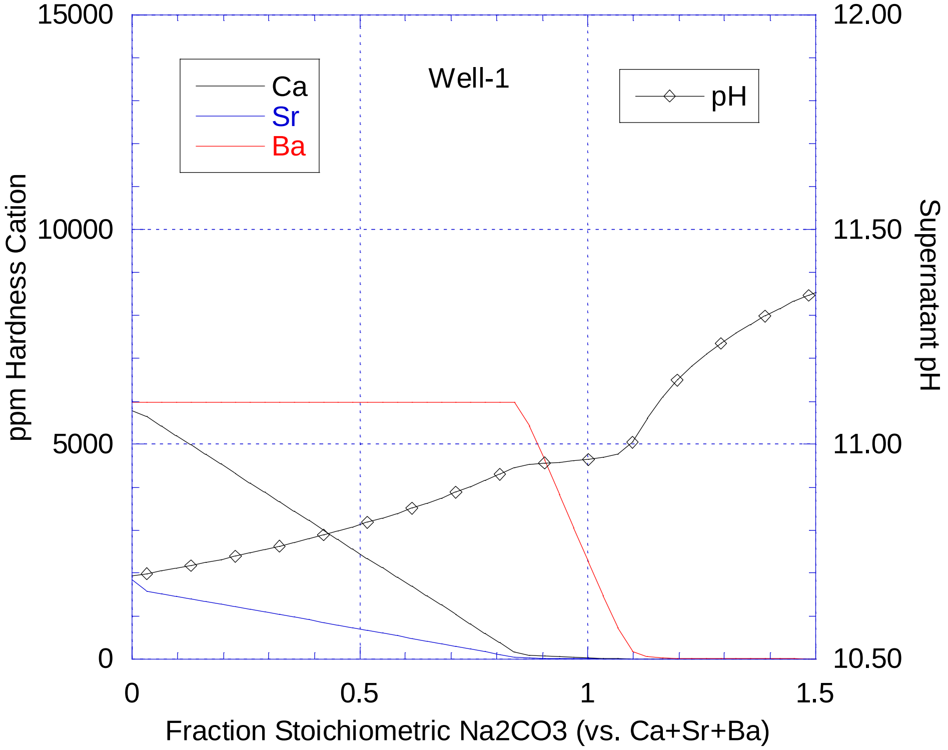

Figure AIV-2. Simulation Results for Well-1 Produced Water

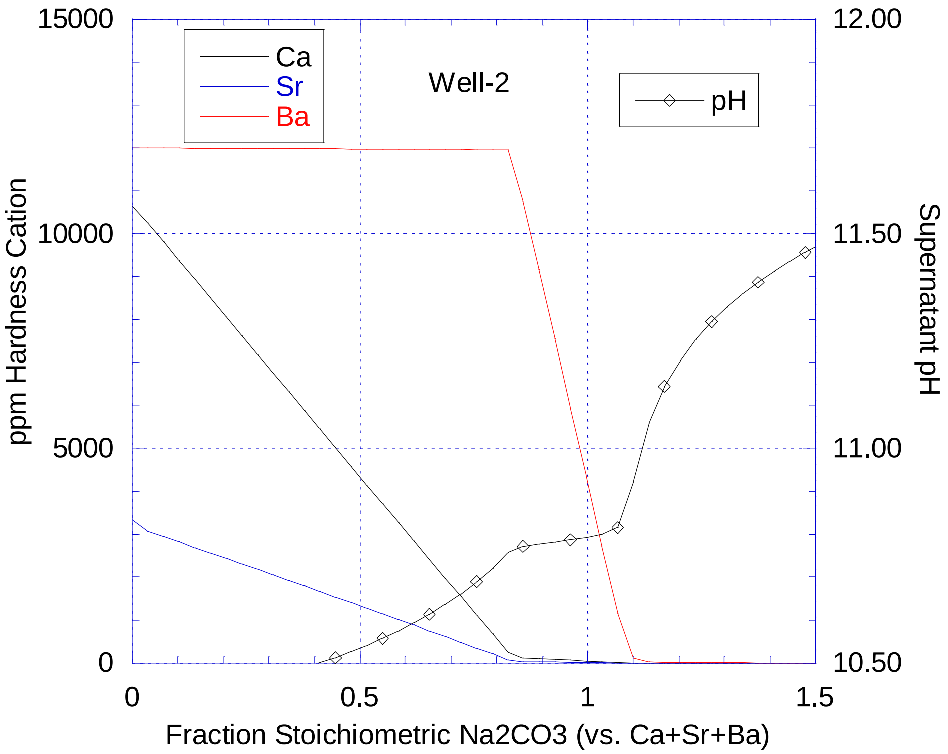

Figure AIV- 3. Simulation Results for Well-2 Produced Water

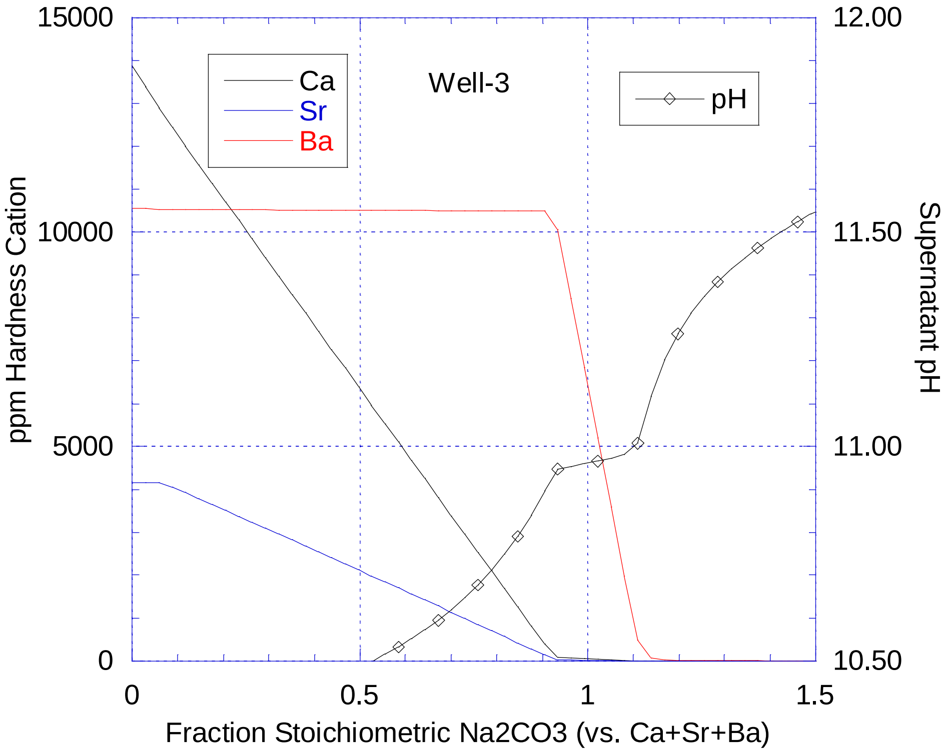

Figure AIV-4. Simulation Results for Well-3 Produced Water

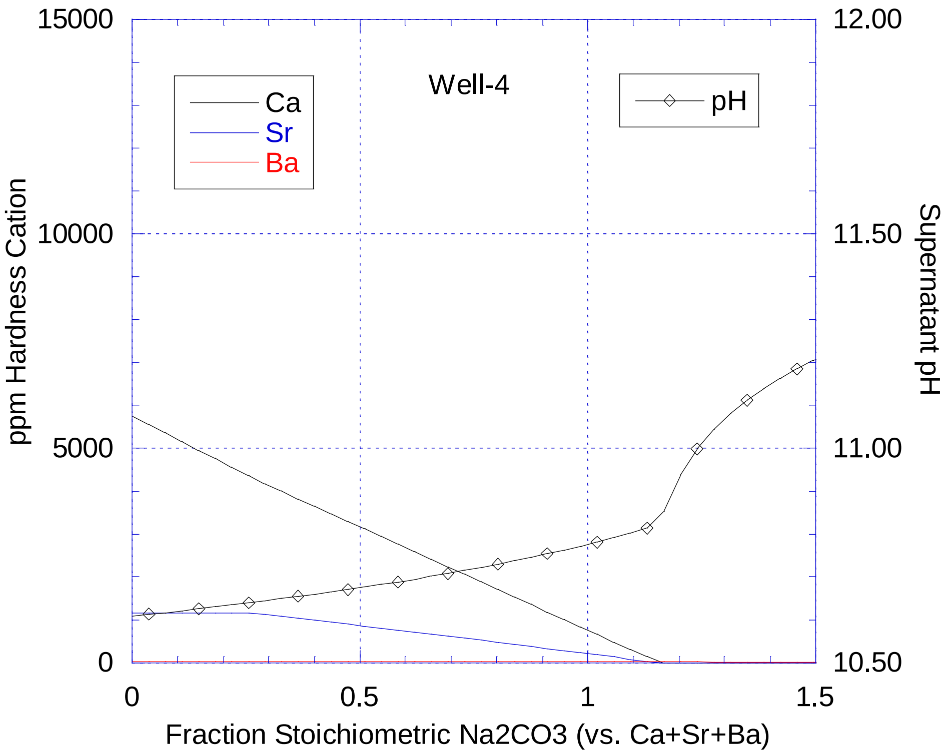

Figure AIV-5. Simulation Results for Well-4 Produced Water

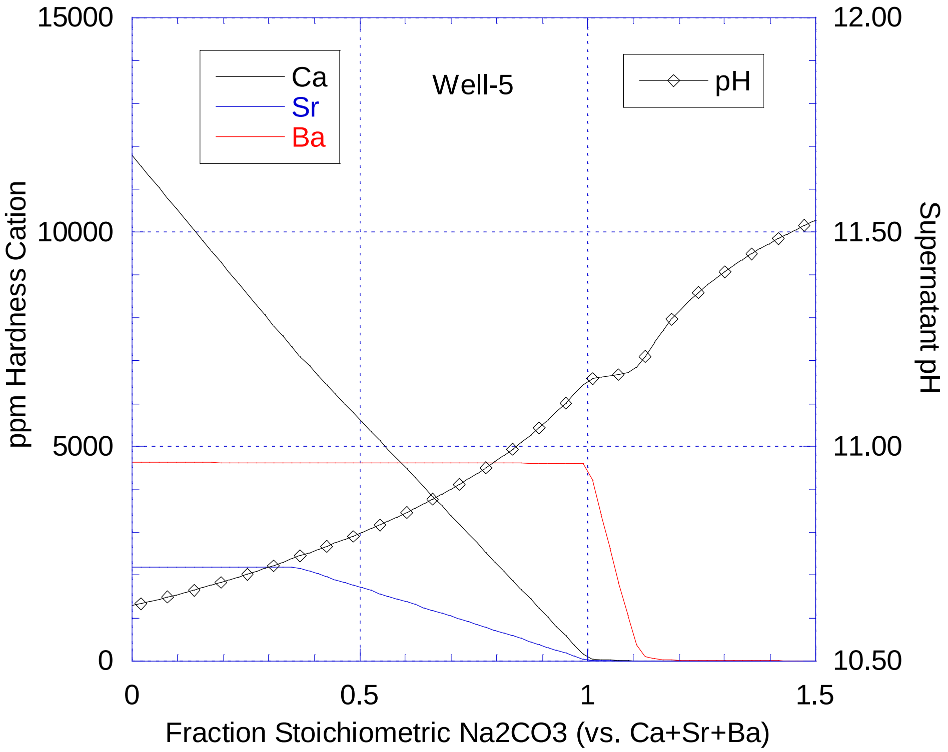

Figure AIV-6. Simulation Results for Well-5 Produced Water

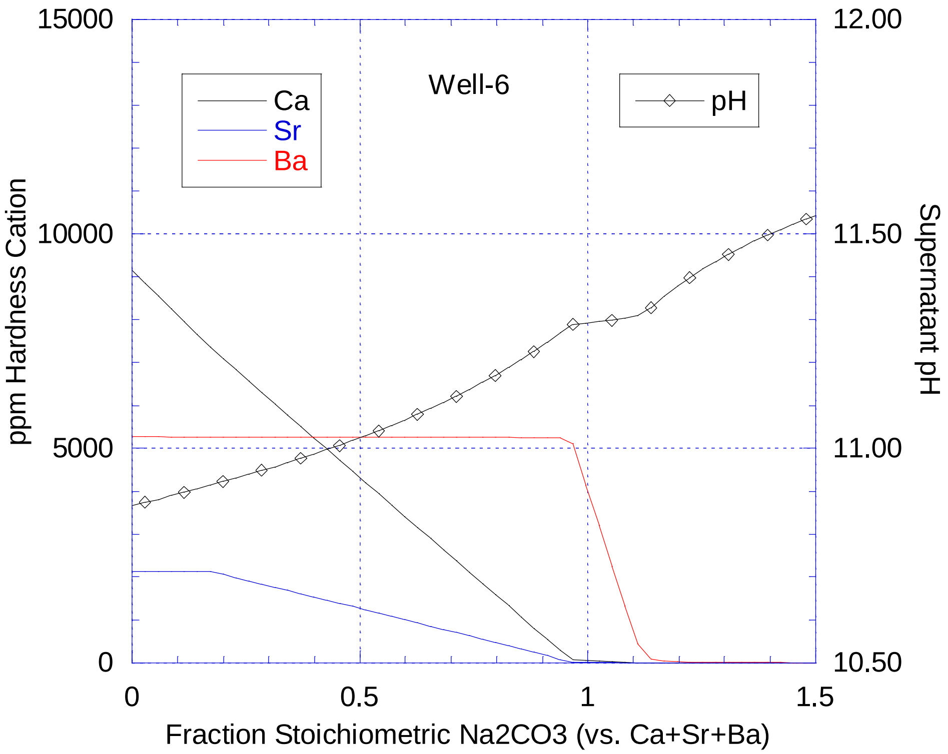

Figure AIV-7. Simulation Results for Well-6 Produced Water

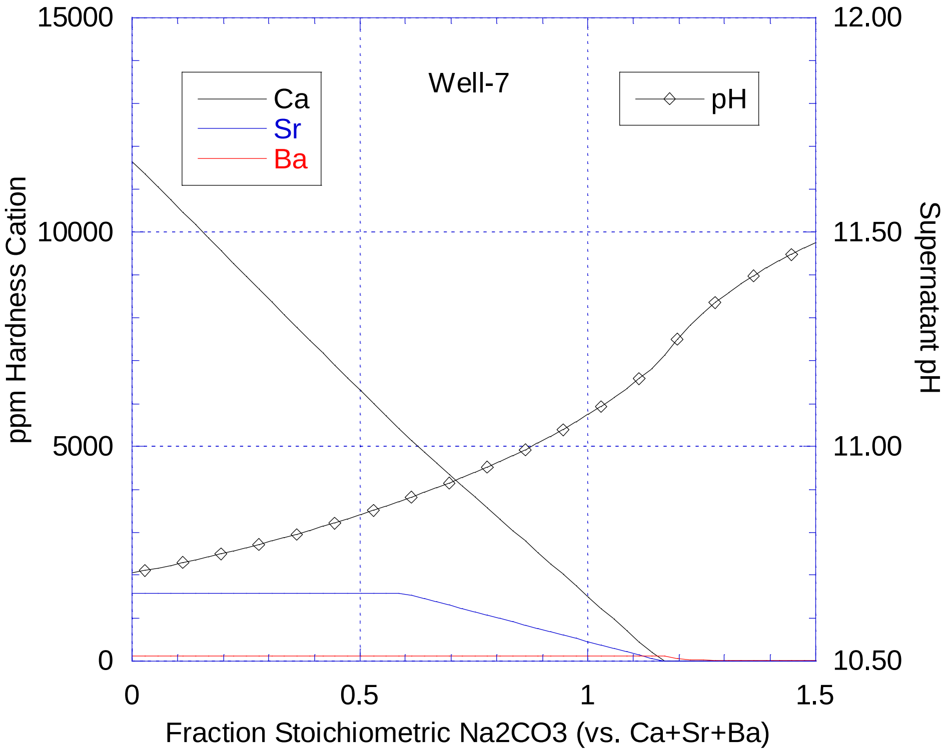

Figure AIV-8. Simulation Results for Well-7 Produced Water

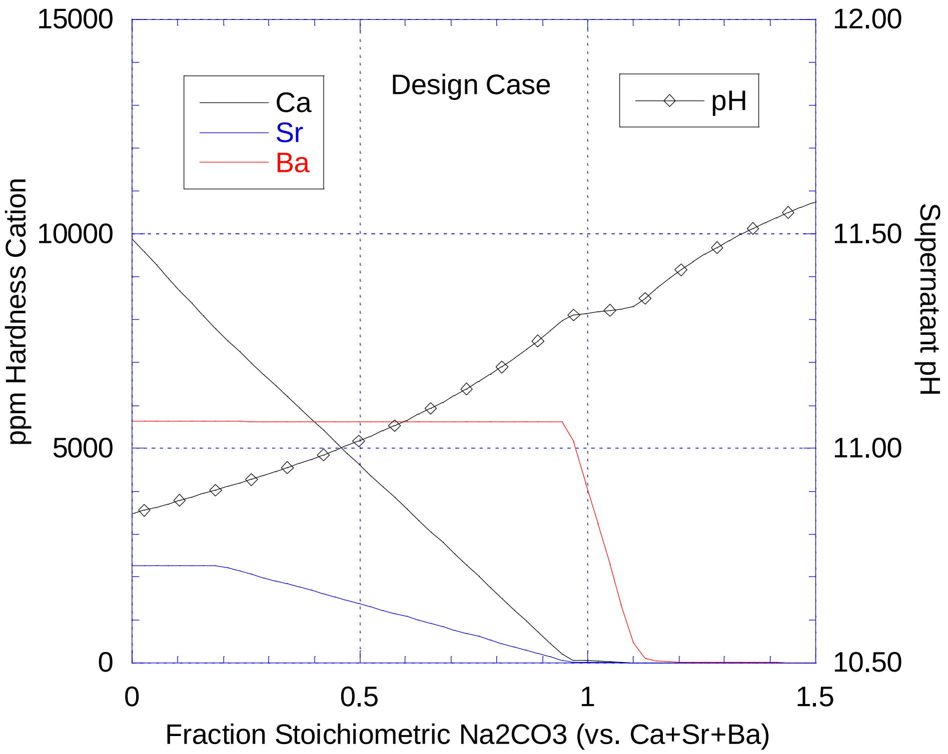

Figure AIV-9. Simulation Results for the Design Case Produced Water

B. Experimental Results for Modified Lime-Soda Process

This section gives details of the experiments that were conducted to demonstrate the modified lime-soda process for softening produced water. We conducted all experiments under ambient conditions, using a magnetic stir bar for agitation. We utilized reagent grade Na_2CO_3, $Ca(OH)_2$, and NaOH for these experiments. The pH was measured with a Thermo-Scientific Orion Five-Star pH meter and an Accumet 13-620-631 pH electrode. All experiments were conducted using Well-5 produced water.

1. Experiment 20110816 with Well-5 Produced water

We added one liter of Well-5 produced water to a 2-liter beaker and placed the beaker on a stir plate. The initial pH of the solution was 5.68. To this solution, 43.29 gm 10 wt% $Ca(OH)_2$ solution was added, which increased the pH to 10.92 and precipitated the magnesium as $Mg(OH)_2$. Then, 212.92 gm of 20 wt% Na_2CO_3 solution was added to the agitated mixture in ten 10 mL increments. This is enough Na_2CO_3 to precipitate all of the calcium, strontium, and barium. Each increment was added essentially instantaneously. Approximately two minutes elapsed between Na_2CO_3 additions. A sample was withdrawn from the beaker after every other Na_2CO_3 addition for LSC analysis. Table AIV-2 and Figure AIV-10 show the LSC results for the filtrate for each amount of Na_2CO_3 added.

Table AIV-2. Results for Experiment 20110826 with Well-5 Produced water

grams Na_2CO_3 (dry) added	mole Na_2CO_3 per mole Ca+Sr+Ba	mole Na_2CO_3 per mole Ca+Sr	Counts/min Above background	Fraction feed counts/min remaining
0	0	0	13.95	1
4.26	0.11	0.113	12.95	0.93
8.52	0.21	0.227	10.58	0.76
12.78	0.32	0.340	9.08	0.65
17.03	0.42	0.454	8.75	0.63
21.29	0.53	0.567	5.35	0.38
25.55	0.64	0.681	5.25	0.38
29.81	0.74	0.794	5.92	0.42
34.07	0.85	0.908	3.55	0.25
38.33	0.95	1.021	3.38	0.24
42.58	1.06	1.135	2.48	0.18

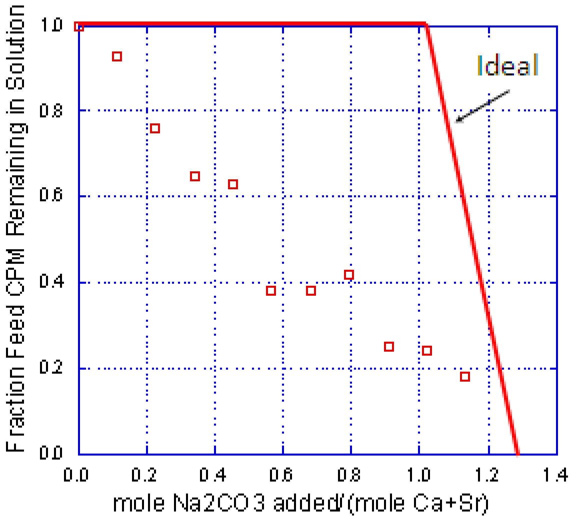

Figure AIV-10. LSC Results for Experiment 20110826

2. Experiment 20110901 with Well-5 Produced water

We added one liter of Well-5 produced water to a 2-liter beaker and placed the beaker on a stir plate. The initial pH of the solution was 5.9. To this solution, 37.35 gm 10 wt% $Ca(OH)_2$ solution was added, which increased the pH to 10.62 and precipitated the magnesium as

$Mg(OH)_2$. Then, 424.9 gm of 10 wt% Na_2CO_3 solution was added to the agitated mixture at a constant rate over the course of 316 minutes. This is enough Na2CO3 to precipitate all of the calcium, strontium, and barium. Samples of the supernatant were removed periodically and filtered through 0.45µ filters. The residual radium activity of each sample was measured using LSC.

Table AIV-3. Results for Experiment 20110901 with Well-5 Produced water

grams Na_2CO_3 solution added	mole Na_2CO_3 per mole Ca+Sr+Ba	mole Na_2CO_3 per mole Ca+Sr	Counts/min Above background	Fraction feed counts/min remaining
0	0.000	0.000	14.73	1.00
20	0.054	0.060	13.28	0.90
45.46	0.122	0.137	11.8	0.80
89.67	0.241	0.270	12.68	0.86
120.52	0.324	0.363	11.7	0.79
201.01	0.541	0.605	11.73	0.80
300.58	0.809	0.905	9.38	0.64
322.08	0.867	0.970	11.22	0.76
335.55	0.903	1.011	8.73	0.59
348.97	0.940	1.051	9.78	0.66
389.34	1.048	1.173	9.27	0.63
403.63	1.087	1.216	8.33	0.57
424.9	1.144	1.280	5.42	0.37

Table AIV-3 and Figure AIV-11 show the results of this experiment. Ideally, the fraction radium activity remaining in solution, as measured by the fraction of the feed counts/minute above background (column 5) remaining in solution, would be unity until the number of moles of Na_2CO_3 added equals the number of moles of Ca^{++} + Sr^{++} in the feed solution, followed by a decrease to zero as the number of moles to Na_2CO_3 increases to about 14% above the number of moles of Ca^{++} + Sr^{++} + Ba^{++} in the feed solution. The 14% molar excess carbonate value is based on the Aspen/OLI simulation results for Well-5 produced water (Figure AIV-6). According to the simulation, with 14% molar excess Na_2CO_3 addition, the residual barium concentration in solution is 59 ppm/w, which corresponds to a reduction of about 99% vs. feed concentration. Although the data show that this *ideal* behavior was not achieved, it is asserted that with improved agitation and other methods such as seeding and the judicial use of antiscalants, the ideal behavior may be approached closely enough to warrant further development. In this experiment, since it is known that radium and barium coprecipitate as carbonates, the fraction barium precipitation behavior may be inferred from the fraction radium precipitation[1].

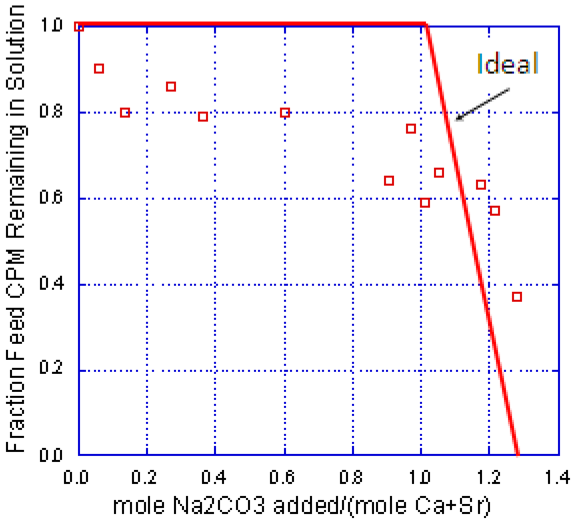

Figure AIV-11. LSC Results for Experiment 20110901

3. Experiment 20110708 with Well-5 Produced water

This experiment utilized NaOH to precipitate Mg, Ca, and Sr as the corresponding hydroxides, followed by Na_2CO_3 to precipitate Ba and Ra as the carbonates. One liter of Well-5 produced water was added to a 2-liter beaker and agitated with a magnetic stirrer. Six aliquots of 50 wt% NaOH (7 mL per aliquot) were sequentially added to the beaker. After each addition, the mixture was allowed to agitate for 2-3 minutes. Then a sample was withdrawn, filtered, and prepared for LSC analysis. The LSC analyses were conducted on the day of the experiment and two weeks later (reported here). After the last NaOH addition, the slurry was filtered through a 1μ glass filter to remove the precipitate. The filtrate was added to the 2-liter beaker and agitation was restarted. Then a series of six aliquots of 20 wt% Na_2CO_3 solution were added in the same manner, with sampling after each increment.

Table AIV-4 and Figure AIV-12 show the results of this experiment. Here, the radium activity stays in solution throughout the course of the NaOH addition.

Table AIV-4. LSC Results from Experiment 20110708

Mole NaOH/ per mole Mg+Ca+Sr	mole Na_2CO_3 per mole Mg+Ca+Sr	mole NaOH/2+Na_2CO_3 per mole Mg+Ca+Sr	Counts/min Above background	Fraction feed counts/min remaining
0	0	0	54.3	1
0.166	0	0.166	52.43	0.966
0.332	0	0.332	50.48	0.930
0.498	0	0.498	51.4	0.947
0.664	0	0.664	51.35	0.946
0.830	0	0.830	49.1	0.904
0.996	0	0.996	50.25	0.925
0.996	0.023	1.019	45.15	0.831
0.996	0.046	1.042	42.06	0.775
0.996	0.069	1.065	36.7	0.676
0.996	0.092	1.088	33	0.608
0.996	0.115	1.111	31.25	0.576
0.996	0.138	1.134	23.81	0.438

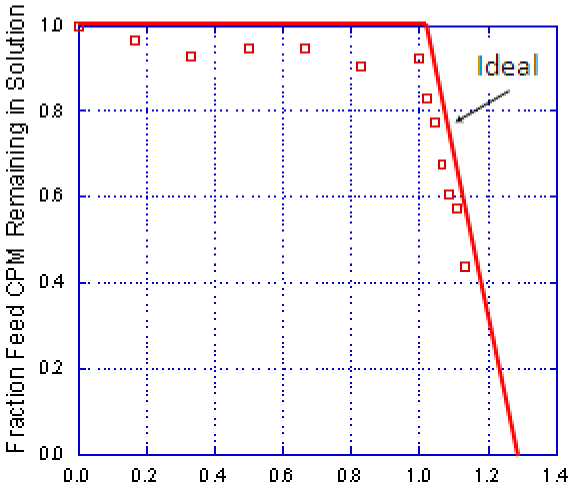

Figure AIV-12. LSC Results for Experiment 20110708

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[1] Kirby, H.W. and Salutsky, M., The Radiochemistry of Radium, National Academy of Sciences, 1964.