Final Report

To:

The University of Wisconsin System
Ground-Water Research Program
on the Project:

"In situ removal of Fe, Mn and Ra

from ground water"

by:

E.R. Christensen [1,3]

and D.S. Cherkauer [2,3]

1. Associate Professor of Civil Engineering

2. Professor of Geosciences

3. Scientist at Center for Great Lakes Studies
   all at the University of Wisconsin-Milwaukee

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SUMMARY

Radium is a naturally-occurring radioactive material found in some ground water in Wisconsin. It has been implicated in human health problems when it is ingested. Iron and manganese are two nuisance constituents of ground water which cause discoloration and taste problems.

Previous studies have shown that in ground-water aquifers of appropriately high permeability, iron and manganese can be removed in situ (directly in the aquifer) by injection of oxygenated water. The process, called Vyredox[TM], avoids the need for expensive, above-ground water treatment to remove these 2 metals. Other studies have noted that in standard water treatment facilities, radium often coprecipitates with the oxides of iron and manganese. It was the premise of this study, therefore, that if iron, manganese and radium occur together in an aquifer in undesirable concentrations then perhaps in situ oxidation could serve as a viable, cost-effective means to remove all 3.

The purpose of this project was to examine that viability. Specifically, we sought to determine: first whether these were ground-water systems in Wisconsin where all 3 elements occurred in elevated concentrations, and second whether radium will coprecipitate with iron and manganese in ground-water aquifer The second objective also required development of a procedure for the determination of low-level radium activity in samples.

The study has shown that existing data allow the identification of only one area in the state where we anticipate that the in situ process might be effective. That is an area ranging from Marathon to Adams Counties in central Wisconsin, where the glacial aquifer has high Fe and Mn and bedrock aquifers show high Ra. Because of their low permeability and greater depth, bedrock aquifers generally won't be efficient locations for injection, so in this area high - Ra water would probably need to be drawn from the deeper aquifer, aerated and injected in

the glacial aquifer to produce in situ removal of all three metals. The viability of this 2 step process was not investigated. There may be other parts of the state where elevated radium coexists with high iron and manganese, but too few radium analyses have been published to identify them.

Investigation of the radium coprecipitation phenomenon was not particularly successful. The findings from the experiments showed that chemical recovery of the radium in samples was too low to produce reliable results. No in-depth investigation about why there was such poor quantitative recovery of radium, so no definite conclusion could be drawn. However, there is a strong indication from the data that the primary loss of radium was due to cation exchange. Attempts were made to overcome the cation exchange problem by coprecipitating radium with barium sulfate. Again, radium recovery was inadequate, due to incomplete removal of sulfate ion in the anion exchange process. Further adjustments produced no better than 6% chemical recovery. This series of trials indicates chemical recovery of the suggested procedure, is qualitative and not quantitative. The losses of radium activity ranged from 75-94%. However, a detailed analysis is needed in order to quantify and confirm the losses of the radium during the processes. As a consequence of the lack of success of developing an efficient means to detect radium, the project could not address the question of whether radium coprecipitates with iron and manganese in ground water.

Regardless, we are unable to positively identify many areas in Wisconsin where in situ coprecipitation would be particularly promising. And in lieu of the USEPA's recent proposal to raise the radium standard for drinking water, it appears the issue is no longer as urgent as it was at the time of the proposal. Very few public water supplies will exceed the new radium standards so removal will be unnecessary.

ABSTRACT

This project was undertaken to determine if radium coprecipitates with iron and manganese during in situ oxidation of ground water and whether there are locations in Wisconsin where the coincidence of these 3 elements in aquifers would make the process a viable treatment option. Concentration of Fe and Mn in public ground-water supplies are high enough to be nuisances and warrant removal in many locations. However, in situ oxidation treatment will be effective only in the unconsolidated Quaternary deposits. Known occurrences of high Ra(>5pci/l) have been mapped, but are extremely spotty. The only area high Fe and Mn coincides with known high Ra is a region between. Marathon and Adams Counties, although the Fe and Mn are highest in the glacial aquifer and the Ra is in the crystalline and sandstone aquifers. In situ oxidation could be effective in this region and is already in use at Rib Mountain. For the overall area defined, Ra-rich water would need to be drawn from the bedrock aquifers, aerated and injected in the glacial aquifer. Other areas of the state might have suitable conditions for in situ treatment, but the Ra data are too sparse to tell.

Determination of the effectiveness of radium coprecipitation was largely unsuccessful because of extremely low Ra recovery levels in the lab experiments. Discussion in this report will emphasize the development of radiochemical processes for the determination of low-level radium activity in water samples along with the tracer (^{225}Ra). The associated problems or difficulties and the results of the recovery of radium from the sample will also be discussed.

INTRODUCTION

High levels of iron and in a water supply cause undesirable staining and taste. Radium (^{226}Ra and ^{222}Rn) causes direct human health risks when ingested and a decay product (^{222}Rn) has been implicated as a health problem when inhaled.

Iron and manganese can be removed in situ from ground water as oxides in a patented process called Vyredox^{TM}, a procedure which eliminates the need for more expensive treatment of the water after it has been pumped from an aquifer. Studies have also shown that radium coprecipitates with iron and manganese oxides (and other forms) in conventional water treatment (Aieta, et al, 1987), although removal never exceeds 50% (William, et al, 1978). If similar co-removal were to occur in the Vyredox process, then in situ oxidation would reduce the levels of 3 undesirable constituents in water supplies in Wisconsin where all 3 elements occur in the ground water.

The objectives of this study were to: 1. document the extent of Fe, Mn and Ra contamination in the ground-water resource of Wisconsin, and 2. investigate the efficiency of Ra co-removal with Fe and Mn - oxides from that ground water. It was originally intended to then extend the project to determining where and under what conditions in situ oxidation would be most effective, but that portion of the project was not funded.

MATERIALS AND METHODS

The distributions of Fe and Mn contents in ground water were developed from previously collected and published data (Syftestad, 1985). All public water supply wells in Wisconsin were subdivided on the basis of the aquifer from which they produce. Four maps locating these wells were developed, one for each of the following aquifers:

1. the Quaternary unconsolidated deposits,
2. the Silurian/Devonian dolomite,
3. the Cambrian/Ordovician sandstone/dolomite, and
4. the Pre-cambrian crystalline rocks.

Combined values of Fe and Mn concentrations were then contoured to produce a map showing the distribution of Fe and Mn concentrations in each aquifer.

The original plan was to produce a similar set of maps for radium concentration. Locations where high Ra coincides with elevated Fe and Mn would be where in situ treatment might be useful. Unfortunately, the data for radium concentrations in Wisconsin's ground water are relatively infrequent, and do not justify statewide contour maps. Instead we produced a single map showing all identified locations of high radium concentrations in well water for comparison to the Fe-Mn maps.

Analyses for radon are more common in ground water than those for radium. For samples on which both Ra and Rn have been analyzed, statistical analysis has been performed to determine whether areas of elevated Rn could be used to indicate where Ra might also be high.

The second objective, determination of the efficiency of Ra co-removal with Fe and Mn, was approached in the laboratory by examining the response of Fe, Mn and Ra in aqueous solution to different, controlled conditions. The concentration of iron and manganese has been measured by atomic absorption spectroscopy using standard procedures. However, radium concentration was measured through a surface barrier detector, with the counting

source prepared from the sample through coprecipitation, ion exchange and electrodeposition.

Conventionally, radon emanation followed by scintillation counters or gamma spectrometers have been used to measure the activity of radium. However, a surface barrier detector with an electroplated source may be preferable for the purpose of this study. Among the reasons are insensitivity of the radon emanation detector, inability to incorporate a yield tracer herein, or an inordinate amount of time necessary for the ingrowth of the daughter radionuclide. By using an alpha detector, a much lower level of activity can be detected (0.01 dpm) and because it counts the isotope itself and not the daughters, a tracer can be incorporated.

A radium source can be prepared in many ways and counted by alpha spectrometry. For example, after coprecipitating the radium in the sample solution along with barium as barium sulfate, a counting source can be prepared directly by laying down a thin layer of the precipitate onto a planchet. However, there are several disadvantages of this method. Because of the use of a carrier (Ba), the spectrum will be degraded through self-absorption. Furthermore, particle recoil and loose precipitate will contaminate the detector, resulting in poor resolution. In addition, losses of the radon through gas diffusion can be significant which resulted in a poor resolution of the spectrum. To prevent these problems, a counting source can be prepared after taking additional steps to separate the radium from the barium. With the carrier free radium solution, a layer of thin, stable radium and resistant to abrasion and leaching, can be deposited onto a steel planchet, thus eliminating the above mentioned problems.

The suggested process involved three steps as shown in Figure 1 (Flow Chart A). First the radium in the sample is coprecipitated with barium as barium sulfate (APHA, 1989; Dickson, et al, 1991; Goldin, 1961). The sulfate that contained

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barium and radium is then dissolved by heating with EDTA.
Secondly, the dissolved sulfate is removed through an anion
exchange column and then the radium is separated from barium
using DCyTA in a cation exchange column (Gleason, 1980). The
carrier free radium is evaporated and dissolved in ammonium
acetate, and is then ready for electrodeposition onto a steel
planchet (Benoit and Harmon, 1988; Garcia and Garcia, 1988;
Gleason, 1980; Masayoshi et al, 1989; Ramon, 1984; Short, 1986).

A tank of about 1.5 x 1.5 ft (approximately 95 L) with a
sealable cap was used as a reactor for simulating the ground
water environment. The ground water material (clay or sand) was
suspended along with the other variables. The control variables
are radium, iron and manganese ion concentration, pH and oxygen.

Analytical reagents were used throughout this work. A 0.05
M DCyTA (cyclohexylenediaminetetraacetic acid, Aldrich) solution
was prepared by diluting 0.1 M DCyTA solution with an equal
volume of saturated boric acid and adjusting to the designated pH
(5.0 and 8.5). The 0.1 M DCyTA solution is prepared by
dissolving 18.2 g of DCyTA along with 4.0 g NaOH in 500 ml
distilled water. ^{226}Ra solution is prepared as described in
standard methods (APHA, 1989), and the tracer ^{229}Th was prepared
in a 1 MHNO$_3$ solution.

There are three steps involved before radium can be counted:
coprecipitation, ion exchange and radium electrodeposition.
First, to a 1 L sample solution (filtered through 0.45 m filter
paper) that had been acidified, 1-2 dpm of ^{229}Th (obtained from
National Institute of Standards and Technology), 5 ml 1 M citric
acid, 2.5 ml of conc. NH4OH, 200 mg of lead nitrate and 10-20 mg
of barium chloride carrier were added. The solution was then
heated to boiling and 10 drops of methyl orange indicator (yellow
at this point) was added. While stirring, 18 N H$_2$SO$_4$ was added
slowly until a permanent pink color was reached and then an
additional 0.25 ml acid was added. The solution was boiled
gently for 5-10 min and allowed to stand until the precipitate

was settled (3-5 hr or more). The clear supernate was decanted and the precipitate was transferred to a 50 ml centrifuge tube with distilled water. After centrifugation, the supernate was decanted. The precipitate was then washed with 10 ml of concentrated nitric acid, stirred and centrifuged again. The washing step was repeated twice to allow for sufficient decontamination After the final wash, 10 ml of distilled water and 2 drops of phenolphthalein indicator solution were added. The solution was stirred to loosen the precipitate and 5 N NH_4OH was added until the solution became red. Then 10 ml of 0.25 M EDTA and 3 ml of NH_4OH were added, and the solution was stirred occasionally for 2 min to dissolve the precipitate. If necessary, the solution was warmed in a steam bath for about 10 min to clear the solution. Concentrated acetic acid was added until the red color disappeared, then 2 drops of bromcresol green indicator solution were added and acetic acid was continually added until the color turned aqueous green (pH 4.5). The solution was then digested in a steam bath for 5 to 10 min. After cooling, the solution was centrifuged and the supernate was decanted. The precipitate was then redissolved with 10 ml of EDTA at a pH ranged between 10-11 (adjusted with 10 NNaOH) while stirring the solution was warmed in a steam bath to aid solution. The solution was then allowed to cool down to room temperature before proceeding to the next step.

Two ion exchangers are used in step 2. The clear solution was passed through an anion exchange resin column (50 mm x 8 mm) in chloride form at a flow rate of 0.2 ml/sec to remove sulfate ions. The column was previously developed by filling the column with about 2 g of resin bead (Bio=Rad AG 1-X8, 100-200 mesh, formate form) and sequentially passing through it 10 ml 6 m NaOH, 20 ml distilled water, 50 ml of 4 M HCl and 20 ml of distilled water. After the solution had drained through the anion exchange column, the effluent, containing barium, radium and EDTA, was collected and its pH was carefully adjusted to 5 (at pH 5, barium

is separated from the EDTA complex and is readily absorbed by the cation resin).

The solution thus prepared was then passed through the cation exchange column (100 mm x 4 mm), in sodium form, for the separation of radium from barium. The cation exchange column was developed by filling the column with 15 g of resin bead (Bio-Rad Ag 1-X8, 100-200 mesh, hydrogen form) and sequentially passing through it 10 ml 6 M HCl, 30 ml saturated NaCl, 20 ml distilled water and then 10 ml of saturated boric acid adjusted to pH 5. The solution was allowed to drain through the column so that barium, EDTA and radium were adsorbed onto the resin in order of increasing selectivity. The resin pH was then adjusted to 8.5 by passing through it 10 ml of saturated boric acid adjusted to pH 8.5. Thymol blue indicator was useful in monitoring the pH. The barium adsorbed onto the column was now removed by passing through it 20 ml of DCyTA/boric acid adjusted to pH 8.5 The resin was then changed to the hydrogen form by passing through it 20 ml of 0.6 M hydrobromic acid or 0.5 M HCl This washing will flush the complexing agent from the column (EDTA or DCyTA). Finally the radium in the resin was eluted with 30 ml of 3M HNO_3. In all cases the flow rate was maintained at 0.2 ml/sec and it was important not to allow the resin to drain dry or to be stirred. This precaution is to allow the reproducibility of the analysis.

In the third step, the isolated radium solution collected from the cation exchange column was evaporated to dryness and dissolved in 10 ml of 0.35 M ammonium acetate electrolyte solution. This electrolyte was prepared by adding 0.35 M ammonium acetate solution to 0.1 M HNO_3 with pH adjusted to 5. The radium solution was readjusted to pH 5.0, if necessary.

A clean 20 ml polyethylene scintillation vial was assembled as shown in Figure 2. The bottom part of the vial was cut out to fit with a polyethylene cap, such that a 1 mm diam. platinum wire with spiral anode end can be suspended through the cap. The

polyethylene cap is equipped with holes to allow the escape of gas generated during the plating process. The cathode was made from a copper plate soldered at the center with a 2 cm long (2 mm diam.) copper wire and snug fitted into the plastic screw cap. The spiral anode end was adjusted to be 10 mm above the steel planchet. After checking for leaks, the electrolyte was poured into the cell and the plating process was started. The process was regulated by a power supply (Lambda model LH125 s), so that the voltage ranged between 11-12 V and the current ranged between 0.4-0.5 Amp. The pH must rise to 8-9 during the first 15 min and the temperature will rise to about 60°C. After plating for at least 3 hours, the plating cell was disassembled and the planchet was washed with distilled water and allowed to air dry. The plated planchet was then mounted and counted on Alpha spectrometer system consisting of an EG&G Ortec 576 surface barrier detector, an ADCAM multichannel analyzer buffer (model 918), a multiplexer-router (model 476), a vacuum pump and an IBM-AT computer.

RESULTS AND DISCUSSION

Fe, Mn and Ra in ground water

Figures 3-6 show the distribution of Fe and Mn, combined, in the public water supply wells of Wisconsin. Whenever multiple samples have been taken at a single location, the value of the average has been plotted. The concentrations have been separated into 4 categories and contoured: high (>1mg/l), moderately high (0.5 to 1.0 mg/l), moderately low (0.1 to 0.5 mg/l) and low (<0.1 mg/l). Only those areas which are in the high category have sufficient Fe and Mn to be deemed undesirable. Only these areas would warrant further investigation for Ra removal by coprecipitation.

It should be added at this point that the in situ oxidation process requires the injection of oxygenated water into the ground-water system. In Wisconsin, the only aquifer which possesses high enough permeability and porosity to allow efficient injection is the Quaternary unconsolidated aquifer. So only the high Fe/Mn areas on Figure 3 would be readily amenable to Vyredox treatment.

For Ra, Figure 7 and Table 1 show all the published occurrences of concentrations in excess of 5 pci/l. The distribution is spotty because so few Ra analyses have been published. The absence of "hotspots" in any area on Figure 6 has little meaning; it could mean that Ra concentrations are low or it could mean no analyses have been published. Only the presence of high Ra is meaningful, and 2 basic trends are apparent. Many wells in eastern Wisconsin which are completed in multiple aquifers and some wells in north-central Wisconsin in the crystalline or sandstone aquifers have high Ra concentrations.

In eastern Wisconsin, the multiple aquifers are the Silurian/Devonian dolomite where present and the Cambrian/Ordovician dolomites and sandstones. These two aquifers

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are separated by the Maquoketa Shale, generally recognized as a
Ra source. These wells are in aquifers that are too deep or too
tight for in situ treatment to be effective, so this region
probably does not warrant further investigation.

In central Wisconsin, there are fewer incidences of high Ra
reported in the area outlined on Figure 7, but conditions may be
more appropriate for in situ treatment. Several wells in the
crystalline aquifer exhibit high Ra. Wood County also happens to
be a location where that aquifer has high Fe and Mn (Figure 6).
The sandstone aquifer Adams County has both high Ra (Figure 7)
and Fe and Mn (Figure 5). Again the hydraulic properties of
these two aquifers probably preclude in situ treatment, but the
high radium wells tend to be in locations where the specific
bedrock aquifer is directly overlain by glacial sediments. It is
conceivable therefore, that treatment might be viable within the
Quaternary material above the high-radium aquifer. Some portions
of the glacial aquifer in this area do possess high enough Fe/Mn
concentrations (Figure 3) to allow in situ removal if deeper
aquifer water were injected in it. This possibility bears
further investigation, but that is beyond the scope of this
study.

Because Rn analyses have been done more commonly than Ra, an
attempt was made to correlate the two. The attempt is confined
to the north-central part of Wisconsin where Fitzgerald's (1990)
data base provides the best information and where Figure 6 shows
there may be a potential for unobserved Ra highs. A correlation
is anticipated because ^{222}Rn is derived from the decay of ^{226}Ra.
However, because the half-lives of these isotopes differ markedly
and because Rn analysis is commonly done immediately while the
sample is stored before Ra analysis, the relation may be masked
by other factors.

Fitzgerald's (1990) samples from Marathon County for which
both Ra and Rn Analyses were done were correlated (Figure 8). A
log-log relation does exist with a correlation coefficient of

0.87 and a significance level of 99%. Using this relationship, it can be seen that samples with a Ra concentration exceeding 5pci/l should contain Rn roughly in excess of 27,000 pci/l. Wells with Rn > 28,000 pci/l could then be added to the list of Ra "hot spots", although these additions are very tenuous, because no Ra analyses have been done.

Fitzgerald (1991) lists the wells in the north central part of the state for which Rn analyses are available. Of these, there are 5 that have high enough Rn for us to suspect that Ra may exceed 5 pci/l. They are:

Eau Pleine, Marathon Co		33,000 pci/l
Rietbrock,	"	28,000
Spencer,	"	38,000
Texas,	"	32,000, and
Wausau,	"	130,000

The latter 2 were already identified by Ra analyses directly, so the Rn data only allow inclusion of 3 more sites on Figure 7. All the high Rn wells are completed in the crystalline aquifer, generally portions of the Wolf River group. This group of rocks, which extends northeastward from Marathon County to northern Oconto County is potentially another area where high Ra concentrations might be found, but there is not much iron or manganese in the overlying glacial aquifer.

The primary conclusion that can be drawn is that there is only one area within Wisconsin where high Fe, Mn and Ra concentrations in ground water have all been shown to occur, an area stretching from Marathon County in the north to Adams and Juneau County in the south. Within this area, the high Ra occurs in bedrock aquifers, while the Fe and Mn are in the glacial aquifer. Water would have to be drawn from the deeper aquifers and then aerated and injected in the glacial aquifer in order to achieve in situ removal of the 3 metals. Whether such a system is feasible has not been addressed; it is beyond the scope of this project.

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Laboratory investigation for Ra co-removal.

Initially, the first attempts were intended to check the chemical yield of the electrodeposition of standard ^{226}Ra solution. But, since the standard solution of radium had Ba carrier which interfered with the electrodeposition of radium, a separation of barium from radium through a cation exchange column was necessary. The separated radium was then electrodeposited and counted. The results are not favorable, showing about 25% chemical recovery (Table 2). The spectrum of the alpha-ray of radium can be seen in Figures 9 and 10. Possible problems could be incomplete separation in the cation resin, absorption losses of radium to the glassware and low chemical yield in the electrodeposition.

The objective of the next attempt was to see how much ^{226}Ra can be recovered through the total simulation, taking account of the low chemical yield in the cation exchange and electrodeposition. To meet this objective, ground water was simulated in a reactor by adding distilled water along with aquifer material and ^{226}Ra standard solution, and the mixed solution was then suspended in the reactor by a rotating blade. The final concentration of ^{226}Ra was 8 pci/l, and the pH of the solution was conditioned to about neutral. Sampling was done using a vacuum pump filter with 0.45-um membrane filter paper. The sample solution was acidified and followed by coprecipitation and solubilization of barium sulfate.

However, a problem was encountered after the solubilized barium sulfate solution was passing through anion exchange column. There was difficulty in trying to bring the pH of the effluent collected from the anion exchanger down to pH 5 as required for cation ion exchange. Theoretically, the effluent collected from the anion exchange column should be in chloride form which should make H adjustment easy. In contrast, the

effluent collected form the anion exchange column precipitated as the pH was lowered to 5. After personal communication with Dr. Geoffrey Gleason (retired professor who developed the method for the separation of radium from barium using DCyTA), the conclusion was made that sulfate ions were not completely removed through the anion resin. A series of corrections were tried to achieve complete removal of sulfate ions through the anion exchange column, but none eliminated the problem. Possible solutions to the problem would be switching to NaCl instead of HCl for the development of the anion ion resin in chloride form (to reduce the acidity of the resin), or lowering of the pH of the solubilized barium sulfate to pH 7, and passing through the anion resin 2 or 3 times. Another explanation for the discrepancy could be losses of radium in the anion exchange.

Since there was not much success in removing sulfate ions in the anion exchange resin, a new attempt involving converting barium sulfate to barium carbonate by heating it in saturated sodium carbonate was tried. The procedure of this attempt is shown in the flow chart B of Figure 1. With out resorting to EDTA for solubilization of barium sulfate, the converted carbonate from sulfate can be easily dissolved in 4 M HCl and passed through the anion exchanger, previously prepared in chloride form by a final wash of 4 M HCL, to remove the carbonate ions And the effluent, from the anion exchanger, is then evaporated and dissolved in 0.5 MDCyTA/Boric acid solution buffered to pH 5. The solution was then passed through the cation exchange for separation of radium from barium. The final eluted radium solution is then evaporated and dissolved in 0.35M ammonium acetate buffered to pH 5 and electrodeposited and counted. The result was better, but the overall recovery 0.5% (Table 2) was still unacceptable. The alpha ray spectrum can be seen in Figure 11. The problems with this attempt might be due to the interference of carbonate ions in cation exchange, since

carbonate is not readily displaced by the chloride ions in the anion resin.

Another alternative was tried, modifying the conversion from barium sulfate to barium carbonate. The subsequent procedure is shown in flow chart C of Figure 1. The converted carbonate was dissolved in 1 M HCl, then 5 ml of 4 M ammonium acetate and 10 ml 25% sodium chromate were added. The pH of the solution was then adjusted to 7 to precipitate the barium as barium chromate along with the radium. The barium chromate was then dissolved in 10 ml 4 M HCl and passed through the anion exchanger, previously prepared in chloride form by a final wash of 4 M HCL, to remove the chromate ion. The effluent collected was then evaporated and dissolved in DCyTA/Boric acid solution buffered to pH 5. The solution was then passed through the cation exchange column for the separation of radium from barium. The final eluted radium was then evaporated and dissolved in 0.35 M ammonium acetate buffered to 5 for electrodeposition. The chemical recovery was better (6.4%) than any other trials, as shown in Table 2, but still not satisfactory. The alpha-ray spectrum is shown in Figure 12.

For checking the chemical yield, ^{229}Th in equilibrium with ^{225}Ra was used as a tracer without milking ^{225}Ra from its parent ^{229}Th (National Institute of Standards and Technology). The ^{225}Ra nuclide was used because it does not occur in nature and does not produce radon isotope which may escape form the counting source. It cannot be measured directly by alpha spectrometer, but its daughters ^{225}Ac($T_{1/2}$ = 10 d), ^{221}Fr ($t_{1/2}$ = 4.9m) and ^{217}At ($t_{1/2}$ = 3.2x10^{-2}s) can be detected after some time (about 10 days). The spectrum of the ^{225}Ra series, using the same plating procedure, is shown in Figure 13. None of these emitters interfered with the ^{226}Ra series.

A sample solution incorporating ^{226}Ra tracer was then run through the chemical process, electrodeposited and counted. The spectrum is shown in Figure 14. Apparently, only ^{226}Ra series was

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detected with 0.8 recovery of ^{226}Ra, while none of the ^{225}Ra series was detected. The possible reason of no alpha-ray spectrum from the ^{225}Ra series may be the extent of losses in the process and the small quantity of ^{229}Th used.

CONCLUSIONS

Successful application of Vyredox™ to remove radium from ground water requires coincidence of four factors:
1. high concentrations of iron and manganese,
2. in a shallow, high permeability aquifer,
3. which also has concentrations radium in excess of 5pci/l, and
4. coprecipitation of the radium on iron and manganese oxides in ground water.

This study has been able to identify extensive areas of iron and manganese concentrations (combined) in excess of 1 mg/l in all major aquifers, so condition 1 is extensively satisfied. Condition 2 restricts the application to permeable portions of the Quaternary glacial deposits, but extensive areas of high Fe and Mn occur in the deposits.

However, identification of high radium concentrations in Wisconsin's ground water was only marginally successful. High concentrations have been published for several dozen water supply wells in the eastern and north-central parts of the state, but no wells in the Quaternary aquifer are in this group. Several wells in central Wisconsin show high radium in the crystalline or sandstone aquifer where it is directly in contact with glacial deposits, but water would probably need to be transferred from the bedrock to the unconsolidated aquifer for application of Vyredox. The main problem is the paucity of published radium analyses. More favorable sites may exist, but they cannot be identified with published data and it was beyond the scope of this project to run the statewide sampling that would be needed to overcome this deficit. Attempts to identify more hotspots using the more extensive radon data base were also unsuccessful. We conclude here that only the area from Adams to Marathon Counties served by bedrock aquifers overlain by glacial deposits

is a region where in situ oxidation might be applied to radium removal.

The study was unable to demonstrate that the fourth condition can be met experimentally. The wide variety of methods tried to separate and quantify radium only attained a maximum chemical recovery of 25%, an unacceptable value. Thus, it has been concluded from these numerous trials that the radium in the sample is not effectively recovered by the procedures used. In addition, it is unclear as to where in the chemical process the radium is lost. From the data, there is an indication that significant losses occur during the cation exchange process. Therefore, if the recovery of the chemical process could be improved, it could be used to determine low-level ^{226}Ra in environmental samples.

As a ancillary note, an attempt was made to measure radium by gamma spectrometry (^{226}Ra, $t_{1/2}$=1600 yrs, 186 kev). The precipitate of barium and radium sulfate prepared by coprecipitation method was gamma counted (Jacqueline, et al, 1981; Jiang & Holtzman, 1989). The measurement of ^{226}Ra looked very promising based on a 1 L sample with 9.3 pci ^{226}Ra activity. The detection limit for a 1 L sample is of the order of 0.5 pci. Sufficient counts (about 800) were obtained in less than 24 hours.

We are unable to conclude, however, that in situ oxidation will have any significant usefulness as a means of reducing radium in Wisconsin's ground water to drinking water standards. Furthermore, in view of the proposed raising of that standard by the USEPA, to a level above most supplies in Wisconsin, the issue has probably become moot.

REFERENCES

Aieta, E.M., J.E. Sirgley, A.R. Trussell, K.W. Thorbjarnarson and
J.J. McGuire, 1987 Radionuclides in drinking water: an
overview AWWA Journal, April, p. 144-152.

APHA, AWWA and WPCF, 1989. Standard methods for the examination
of water and wastewater. 17th Ed., Washington, D.C.

Benoit, G. and H.F. Harmon, 1988, Improved methods for the
measurement of ^{210}Po, ^{210}Pb and ^{226}Ra. Limnol. Oceanogr.
33:1618-1622.

Dickson, B.L., R.L. Meakins and C.J. Bland. Radium removal from
Australian SPA waters. To be published in Bull Aust.
Radiation Protection Soc.

Fitzgerald, C, 1991. Naturally occurring radionuclides in ground
water of North Central Wisconsin. WI Dept. of Natural
Resources in house publication.

Garcia-Tenòrion and Garcia-Leon M 1988. ^{226}Ra determination by
electrodeposition. The Sci. Tot. Env. 69:225-238.

Gleason, G. 1980. An improved ion exchange procedure for the
separation of barium from radium p. 47-50. In WS Lyon [ed].
Radioelement analysis: Progress and problems. Ann Arbor
Sci (1979).

Jacqueline, M. S.M. Willard and T.K. Philip, 1981. Gamma-ray
spectrometry for determination of Radium-228 and Radium-226
in natural waters. 53:1885-1889.

Jiang, Huixaia and R.B. Holtzman, 1989. Simultaneous
determination of ^{224}Ra, ^{226}Ra and ^{228}Ra in large volumes of
well waters. Health Physics 57:167-168.

Masayoshi, Y., Kazuhisa, K. and Kaoru, U. 1989. Determination of
low-level ^{226}Ra in environmental water samples by alpha-ray
spectrometry. Radiochimica. Acta. 46:137-142.

Roman, D. 1984. Electrodeposition of radium on stainless steel
from aqueous solution. Int. J. Appl. Radiat. Isot. 35:990-
992.

Short, S.A. 1986. Measurement of all radium isotope at
    environmental levels on a single electrodeposited source.
    Nucl Inst. Meth. in Phy. Res. B17:540-544.

Syftestad, E.P. 1985. Public water supply data book-1985, Wisc.
    Dept. of Natural Resources, 212 p.

William, L.B., R.J. Schliekelman, L.B. Dorothy, R.B. Charles and
    M.M. Ira,, 1978. Radium-removal efficiencies in water
    treatment processes J. AWWA. 70:31-35.

Table 1   Water supply wells in Wisconsin with total radium in excess of 5pci/l.

Data are separated into 2 groups, one of wells in a single aquifer and the other of wells in more than one aquifer. Sources: Syftestad, (1985), Fitzgerald (1991).

Radium Hotspots   (single aquifer)

County	Number	City/Town	Rn	Ra(226)	Ra(228)	U	Aquifer
				Radioactivity (pc/l)			
Adams	1	Preston		2.5	3		s
Brown	1	Depere W.W.		~3.8	~3.0		s
	2	Howard		~3.5	~2.4		s
Calumet	1	Sherwood W.W.		~16	~16		l
Dunn	1	Downsville	~600	~8.0	~5.0		s
	2	Menominee W.W.	~928	~3.0	~4.0		s
Green Lake	1	Berlin W.W.		~3.0	~2.5		s
	2	Princeton	~300	~6.1	~3.8		s
Jefferson	1	Jefferson W.W.	~350	~3.1	~2.0		s
Marathon	1	Frankfort		6.4	2.3	19	c
	2	Maine	3400	2.3	3.3	<1.0	c
	3	Texas		4.6	5.9	129	c
	4	Wausau		28.3	2.8	31	c
		"	6906	46.5	10.6	24.7	c
		"	391394	55.1	2.9	162	c
		"	31274	31.3	2.5	88	c
		"	203455	35.5	2.4	105	c
Monroe	1	Tomah W.W.		~4.0	~1.8		s
Outagamie	1	Darboy (SD 1)	206	~3.2	~2.3		s
St. Croix	1	Hudson W.W.	~850	~3.5	~2.5		s
Winnebago	1	Winneconne W.W.		~3.5	~3.5		s
Wood	1	Grand Rapids		1.6	5.2		c
	2	Hansen		8.3	5.1		c

c: crystalline
l: limestone
s: sandstone

Table 1   cont

Radium Hotspots   (mutiple aquifers)

County	Number	City/Town	Rn	Ra(226)	Ra(228)	Aquifer
Brown	1	Allouez W.W.	~400	~5.0	~2.5	lss
	2	Ashwaubenon	~350	~4.0	~2.2	lss
	3	Bellevue	~350	~12.0	~6.0	lss
	4	Green Bay W.W.		~4.0	~2.0	lss
	5	Holland-Kaukana	~190	~16.0	~15.0	sls
Dodge	1	Brownsville	~600	~4.1	~2.5	ls
	2	Hustisford	~250	~6.0	~4.0	ls
Fond du Lac	1	Fond du Lac W.W.	~350	~5.5	~3.0	lsc
	2	Mary Hill Park S.D.	~220	~4.2	~4.0	ls
	3	N. Fond du Lac W.W.	~300	~5.0	~6.0	ls
	4	Taycheedah C.I.	~300	~12.0	~7.0	ls (?)
Jefferson	1	Johnson Creek W.W.	~500	~4.0	~3.0	sl
Kenosha	1	Pleasant Prarie I.P.	103	~5.0	~6.0	lsls
		" T.R.	158	~9.5	~8.0	ls
Marinette	1	Peshtigo W.W.	~280	~3.9	~3.5	ls
Milwaukee	1	Franklin W.W.	~200	~4.5	~4.5	sl
Oconto	1	Oconto W.W.		~5.0	~1.1	ls
Outagamie	1	Kaukana (E&W)	~250	~2.9	~3.2	ls
Racine	1	Caledonia (Caddy Vista)	90	~4.6	~2.1	ls
	2	Racine (Crest View)	~160	~6.0	~3.0	ls
	3	Union Grove	~160	~25.0	~2.8	lssh
	4	Waterford W.W.		~4.5	~2.0	ls
Waukesha	1	Brookfield (Zone 1)		~3.5	~3.0	ls
	2	Eagle W.W.	~350	~5.0	~3.8	ls
	3	Menominee Falls W.W.		~3.5	~2.5	lss
	4	Mukwanago W.W.	~300	~4.9	~3.5	ls
	5	New Berlin W.W.	~150	~4.2	~3.2	lss
	6	Pewaukee Village W.W.	~225	~2.8	~3.0	ls
	7	Sussex	~350	~3.9	~3.0	ls
	8	Waukesha	~250	~4.0	~7.0	ls

c: crystalline
l: limestone
sh: shale
s: sandstone

ex. lssh: limestone, sandstone, shale aquifers used as sources

Table 2   Recovery of ^{226}Ra from sample solution (1 L).

Sample	^{226}Ra added	Number of counts	Counting time	Chemical recovery	Overall recovery*
	(dpm)		(min)	%	%
RA-1[1]	22.2	1236	1000	27.8	5.6
RA-2[1]	22.2	1112	1000	25.0	5.0
RA-3[2]	21.5	503	5000	2.4	0.5
RA-5[3]	22.2	558	3225	3.9	0.8
RA-6[4]	22.2	917	3225	6.4	1.3

[1] ^{226}Ra recovered from cation exchanger.
[2] ^{226}Ra recovered from the chemical process through conversion from sulfate to carbonate form.
[3] ^{226}Ra and ^{229}Th(^{225}Ra) recovered from cation exchanger.
[4] ^{226}Ra recovered from the chemical process through conversion from carbonate to chromate form.
* Detector efficiency about 20%.