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URANIUM MINING IN TEXAS: WHY IS IT DONE THAT WAY?

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"How many years can a mountain exist
Before it's washed to the sea?"

—Bob Dylan, "Blowin' in the Wind"

I. Introduction

The mining of uranium is carried out in widely separated parts of the world, including, surprisingly, the Gulf coastal plains of Texas. The mining method used to actually recover uranium varies depending on ore type, the geology of the area and other local factors. Open pit mining is preferred when the uranium exists in abundant amounts close to the surface. When the uranium occurs in veins deep under ground, box cut or underground tunnel mining is preferred. The most common method employed along the Texas Gulf Coast is called in-situ leaching (ISL). This method leaves the main body of the ore in place and removes the uranium by dissolving it in an appropriate solvent and then pumping it out of the ground. The solvent most commonly used is oxygen-saturated water containing an acid such as sulfuric acid or a base such as sodium bicarbonate. This method obviously requires that the ore body is located in a matrix that is permeable to the solvent. This type of matrix generally has associated groundwater. ISL methods are attractive when the ore is of low grade and other methods are too expensive to be profitable. The downside is that the associated groundwater away from the ore body could be contaminated. Although in-situ leaching is highly regulated both by the state and by the federal government, the regulations that have been followed for more than 30 years appear to be faulty and do not adequately protect the local groundwater from excessive contamination by uranium and radium. Showing that to be true is the main focus of this paper.

Most current U.S. ISL uranium production is from mines in Wyoming and Texas. According to the Nuclear Energy Agency (2008), 38 percent of U.S. uranium reserves are classified as ISL amenable. Thus, the safe and effective use of ISL technology in mining uranium deposits is a potentially critical element in the movement towards energy independence in the United States.

My interest in ISL mining and its problems was originally generated in response to a legal question concerning the validity of reported baseline values of certain chemical constituents, primarily uranium and radium, in the groundwater within a proposed mining permit boundary. These concentrations were submitted by the Uranium Energy Corporation (UEC) as required information in an application to the Texas Commission of Environmental Quality (TCEQ) for a permit to conduct in-situ mining of uranium in Goliad County, Texas. Although the discoveries I have made were obtained from data specific to this mine in Texas, I believe that the results are generally valid for all such mining operations regardless of location.

II. Uranium Mining in Texas

The story begins in the Trans-Pecos region of West Texas. Uranium occurs naturally within the rocks that form the Earth's crust, particularly in granite, volcanic ash, and volcanic lavas. Some deposits occur as uranium-rich veins that formed within granitic magmas, but many deposits are formed when oxidizing groundwater leaches uranium from igneous rocks. The uraninite ore (UO_2) found in the sand layers of the Texas coastal plains is derived from uranium brought to the Earth's surface during intense volcanic activity in the Trans-Pecos region during the mid-Cenozoic era, approximately 48 million years ago. Over the following few million years, the volcanic ash and rock fragments eroded, mixing with sediments that eventually blanketed the Gulf coastal plain. Uranium enriched groundwater, traveling perhaps a few feet per year, transported its radioactive cargo to where it was eventually precipitated between 15 and 30 million years ago in chemically reducing zones. A reducing zone in the aquifer strata is caused by significant amounts of sulfide (iron pyrites, for example) and/or organic material (natural gas and/or oil). When the moving groundwater encounters the reducing materials in this zone, the soluble uranium undergoes a chemical reaction with these materials and precipitates in the pores of the sand, forming an ore deposit. These reducing zones are commonly found in areas such as fault zones where decaying organic products collect and react to remove the oxygen from the system. Soluble metal sulfates such as iron sulfate are also reduced to ores such as pyrite that can also cause soluble uranium salts to precipitate as uraninite ore. The ore remained, hidden by its chemical nature, until it was discovered just over a half century ago. All the while, the

precipitated uranium ore was very slowly radioactively decaying through a series of elements, including radium, and finally to inert lead.

Texas uranium was first discovered in Karnes County, Texas in 1954, as a result of airborne radiometric survey. A number of uranium deposits had been discovered within a belt of strata extending 250 miles from the middle coastal plain southwestward to the Rio Grande. Uranium deposits have been found in various locations across the Texas coastal plain, in the Panhandle and High Plains, and in volcanic rocks of Trans-Pecos Texas. Currently uranium is mined only in geologic formations along the South Texas coastal plain (Galloway 1979; Swanson 1995). This area includes the Carrizo, Whitsett, Catahoula, Oakville, and Goliad geologic formations. Open pit mining began in 1961 and in-situ leach mining was initiated in 1975, but the decreased demand and price of uranium after 1980 brought a sharp decline in all Texas uranium operations. Figure 1 shows the various uranium-bearing formations in the coastal plains of Texas.

To be authorized to engage in ISL mining of uranium in Texas, a company must satisfy certain requirements set by the TCEQ. Texas House Bill 3838, 80th Texas legislature, required the TCEQ to establish criteria for exploratory wells to be permitted by the Texas Railroad Commission. The exploratory wells are to be used to map sites of uranium that are potentially profitable to mine. Prior to mining, however, applications to the TCEQ must be filed to obtain a Class III injection well permit for a designated mining boundary; a production area authorization (PAA); and an aquifer exemption. To satisfy the combined requirements for obtaining the mining and PAA permits, the state of Texas requires the mining company to:

- Provide a detailed description of the production area geology and hydrology.
- Drill "baseline wells" to establish a baseline value for 26 specified groundwater chemical constituents in the production area of the mine. These must be measured and reported before actual mining operations are started.
- Present a proposed plan for the actual mining operations.
- Propose restoration procedures, after mining is completed, for returning the groundwater to its original condition as set by the baseline values measured for the 26 chemical constituents.

Furthermore, prior to mining, the proposed areas to be mined must be exempted from being an underground source of drinking water (USDW). Criteria for exemption are:

- No one currently drinks the water, and
- Until the quality of the groundwater is restored and the exempt status is removed, no one will drink the water because its mineral or geothermal character, its depth or location, or its pre-existing contamination renders it impractical for treatment to make it fit for consumption.

This exemption is initially approved by the TCEQ and is then submitted to the U.S. Environmental Protection Agency (EPA), which must approve this exemption as an amendment to the approved state underground injection control program to protect underground sources of drinking water.

An important point is that if the baseline measurements of any of the 26 designated chemical components is above the EPA maximum contaminant levels (MCL), the aquifer can be designated unfit as drinking water and can be declared exempt on this basis. It would be to the advantage of the mining company for that to be true because the baseline concentrations of uranium and/or radium are almost always measured to be above MCL. Also, it is generally impossible to return the quality of the groundwater to even the elevated original conditions as set by the baseline measurements. Thus, the measured baseline groundwater concentrations of uranium and radium are critical factors in determining the cost of operation and recovery.

It has been assumed that, because the groundwater is in the vicinity of radium containing uranium ore, it is only natural for that groundwater to show high concentrations of the two elements. I believe that to be a false assumption and that natural undisturbed concentrations are a great deal lower than measured and may be below the MCL for both radium and uranium. In this paper, I will show that preexisting elevated levels of uranium and radium in the mining area are artifacts of the standard methods used to establish baseline values for groundwater quality as recommended by the U.S. Nuclear Regulatory Commission.

Historically, thirty-six ISL mining sites have been authorized in Texas since 1975; seven were never mined, one was a tailings project, and one was combined with another property. This leaves 27 mines that were developed by constructing and combining 77 well fields. These 27 mines are termed production authorization areas (PAAs). Currently two of these mines are active in Texas: the Kingsville Dome mine in Kleberg County, operated by Uranium Resources International (URI), and the Alta Mesa mine in Brooks County, operated by Mestena Uranium. Two other ISL mines are in the process of being permitted: Goliad in Goliad County (Uranium Energy Corporation) and La Palangana, a South Texas Mining Ventures property in Duval County (Hall 2009).

Baseline and "amended restoration" values are available for all 27 mines/77 PAAs in TCEQ records. Each record contains a data sheet summarizing pre-mining groundwater baseline data as required for a Texas PAA. Restoration values are initially set as baseline by mine operators selecting the highest average concentration from either the production or mine area as their restoration goal. All PAAs in Texas have had to request, and did receive, amended restoration goals for at least one element after operators have unsuccessfully expended a reasonable degree of effort following established guidelines to restore groundwater.

The U.S. Environmental Protection Agency and the TCEQ have established primary MCLs for the various chemical constituents of potable groundwater. The MCL for uranium is 0.03 milligrams per liter (mg/L) and for radium is 5 picocuries/liter (Pci/L). Of the 77 PAAs from the 27 mines, only 22 PAAs from 13 mines reported final concentration values for uranium and radium. For radium, the baseline range reported from these 22 PAAs was 9.36-429.8 Pci/L and the post-mining restoration range reported was 5.2-149 Pci/L. Thus, 100 percent of the baseline values were above the MCL and 100 percent of the post restoration levels were above the MCL, but 96 percent of the post-restoration analyses were below the locally established baseline value. In the case of uranium, the baseline range for these PAAs was 0.025 to 2.0 mg/L and the post-mining restoration range reported was 0.013-3.02 mg/L. In this case, 95 percent of the baseline values were above the MCL and 86 percent of the post restoration levels were above the MCL, while 68 percent of the post restoration analyses exceeded the locally established baseline value

(Hall 2009). These figures do not show an appropriate level of success in the procedures required and used.

III. The Chemistry of Uranium Mining

Before discussing specific results on baseline measurements of uranium and radium in the proposed Goliad mine, it is appropriate to review a few pertinent facts about uranium, particularly its radioactive decay, its various oxidation states, its solubility as a function of an ambient redox potential, and its relationship to radium.

A. Formation of a Typical Texas Uranium Ore-Bearing Formation

Ore-bearing formations in South Texas are most often comprised of stacked layers of fine to coarse sand and/or sandstone separated from one another by layers of clay, shale, or silt. The sediment making up these formations was carried to its current location by a large system of meandering and braided rivers that flowed across the flat northwest coastal plain to the Gulf of Mexico during the Eocene to Miocene ages, six to 55 million years ago. As the sediment accumulated, it formed layers of intermixed sheets and tabular-shaped deposits. Since the area had little variation in elevation, rivers tended to be rather shallow and wide. Fine to coarse sand was deposited in these riverbeds. Occasionally the rivers would flood, bringing large quantities of silt and clay sediment that was deposited over the large areas of the plain outside of the existing riverbed. Through geologic time, the rivers switched channels back and forth across the coastal plain. Such periodic changes in the flow of the rivers eventually caused the layering of channel fill sand and flood plain clay/silt/shale that characterize these formations (Galloway 2010).

Deposits of uranium are aquifer-controlled ore bodies that form in medium- to coarse-grained sandstone. Oxidizing groundwater leaches uranium from its source rock in the Trans-Pecos and carries it through sandstone until it reaches a reducing environment. An abundance of organic material or petroleum seeps along faults, or an abundance of sulfide mineral in the sediment forms reducing environments. Uranium oxide precipitates in any available rock pore space at the interface between oxidizing and reducing conditions, often forming a curved "roll-front" ore body. This reduction/oxidation front can migrate over time, creating an ore trend that extends for

miles. Numerous ore bodies are sometimes stacked parallel to one another at intervals along this trend, reflecting preferential flow paths in the aquifer. Roll-fronts are the predominant uranium deposit in the coastal plain (Campbell et al. 2007).

The uranium is typically deposited as uranium oxides and, to a lesser extent, uranium silicates. Uranium concentrations generally range from 0.04 to 0.25 percent by weight. Most roll-front deposits are mined through in-situ leaching. This is particularly true of well-sorted fluvial sandstones that have good porosity and permeability and are in confined aquifers bounded by impermeable clays.

In summary, uranium is transformed from a solid form at the volcanic site to a solution wbereby it is transported over hundreds of miles. It eventually reaches a chemical zone that is capable of reprecipitating the uranium and then it stays there in an inert state until it is re-dissolved in the mining process.

B. Chemistry of Uranium

Uranium (U) is the heaviest of the naturally occurring elements with 92 protons and 92 electrons in the neutral atom. Various isotopes also contain different numbers of neutrons. All of the isotopes are unstable with respect to radioactive decay. The most abundant isotope of uranium is U-238, which contains 146 neutrons. Natural uranium is 99.284 percent U-238, which undergoes radioactive decay by a series of alpha and beta particle losses (see Figure 2). U-238 decays to its first daughter element Th-234 with a half-life of 4.468×10^9 years. That is to say, when a pound of U-238 starts to decay, half of it will be gone in 4.468 billion years, roughly the age of our solar system. No wonder it is still fairly abundant. More to the point, if a certain amount of U-238 were deposited 20 million years ago as a precipitated ore sample such as is found in Goliad, 99.7 percent of the original uranium would still be left today. The ore would also include various decay products—most importantly, radium, along with the final end product of radioactively stable lead.

Uranium has a rich chemistry, existing in several oxidation or valence states. It can be found in the form of cations, anions, and complexes with many other chemicals. This is a direct consequence of the fact that uranium has six valence electrons and thus the ability to exist in

several oxidation states depending on ambient conditions of hydrogen ion concentration, pH, and reduction potential, Eh. For example, the most important oxidation states of uranium are uranium(IV) and uranium (VI); their two corresponding oxides are, respectively, UO_2 (uranium dioxide) and UO_3 (uranium trioxide). Other, less common, oxides such as uranium monoxide (UO), diuranium pentoxide (U_2O_5), and uranium peroxide ($UO_4 \cdot 2H_2O$) also exist. The most well-known uranium oxide is U_3O_8, better known as yellow cake or pitchblende. It can be thought of as containing two valence forms of uranium, U(IV) and U(VI).

The most common forms of uranium oxide are U_3O_8 and UO_2. Both oxide forms are solids that have low solubility in water and are relatively stable over a wide range of environmental conditions. Uranium dioxide is very stable and is the form in which uranium is most commonly used as a nuclear reactor fuel. It is also the form of uranium in uraninite, the ore form generally found in Texas coastal plain deposits.

Formally speaking, U(IV) in the form of UO_2 can be converted to U(VI) by the loss of two electrons. The loss of electrons is called oxidation. Electrons can't simply exist in chemical systems so they must be transferred to another chemical to give a stable system. Thus a reaction involving the loss of electrons must be coupled to some other process that gains electrons. Adding these two "half reactions" one obtains, for example, a process for the oxidation of uraninite with oxygen:

$$6H^+ + 1/2O_2 + UO_2 \rightarrow U^{+6} + 3H_2O$$

Note two features of the above process:

1. Hydrogen ions are used up. This would favor the reaction at low pH or, in other words, the oxidation of uraninite ore is pH sensitive.
2. The uranium in a plus-six oxidation state remains in solution until it encounters a reactive reducing agent.

A suitable reducing agent can reduce soluble U(IV) to insoluble U(VI) and precipitate it from the groundwater solution. A reducing agent is a source of electrons. That source, for example, may be a sulfide such as pyrite.

The equation for the reduction of soluble U(VI) to insoluble UO_2 by iron pyrite is

$$4U^{+6} + 12H_2O + FeS_2 \rightarrow 4UO_2 + FeSO_4 + 24H^+$$

In groundwater solution, the uranium is usually complexed with other species to give a rather complicated chemical system. Figure 3 is the phase diagram associated with the above reactions in the presence of carbonate species (commonly used in ISL mining of uranium).

In a highly reducing environment (the absence of an oxidizing agent, such as oxygen) uraninite (UO_2) is very insoluble in water. In pure water with low oxygen tension at a pH of 5.6, a pressure of 750 bar, and a temperature of 270°C, the concentration of uranium in equilibrium with solid UO_2 was reported as $10^{-9.5}$ moles/liter (0.00007 mg/l) (Valsami-Jones et al. 1994). Under normal temperature and pressure and complete reducing conditions of undisturbed ore bodies' concentrations of soluble uranium are reported to be less than $10^{-8.7}$ moles/liter (0.0005 mg/l) (Casas et al. 1998; Rai et al. 1990). This value can change depending on pH and the presence of complexing agents in the groundwater, but that is usually rather insignificant. The EPA uranium concentration standard for drinkable groundwater is $10^{-6.9}$ moles/liter (0.03 mg/l), a concentration much greater than to be expected in an undisturbed uranium ore body.

C. Chemistry of Radium

Radium (Ra) is a radioactive chemical element with an atomic number of 88. That is, it contains 88 protons in the nucleus and 88 electrons surrounding the nucleus. Its appearance is almost pure white, but it readily oxidizes on exposure to air, turning black. Radium is an alkaline earth element similar in chemical properties to barium (Ba). It has four isotopes, all of which are radioactive. The most stable isotope is radium-226, which has a half-life 1590 years. As one of the more stable radio-decomposition products of U-238, radium-226 is found in trace amounts in ores such as uraninite. It is extremely radioactive and decays into radon and finally decays to a stable end product, lead (Pb).

Marie and Pierre Curie first discovered radium in 1898, and it served as the basis for identifying the activity of various radionuclides. One curie of activity equals the rate of radioactive decay of

one gram (g) of radium-226. Equally, one picogram of pure radium has an activity of one picocurie, the most common unit for reporting radium concentrations.

Radium is widely distributed in small amounts in the Earth's crust. The EPA maximum contaminant level (MCL) for radioactivity in drinking water is set at the level of a 1 in 10,000 risk of a fatal cancer if two liters of water per day are consumed for 70 years. The MCL for the concentration of total dissolved radium, which is defined as the sum of Ra-226 and Ra-228 concentrations, is 5 pCi/l (EPA 2000). Levels found in groundwater normally do not exceed 1 pCi/l from Ra-226. Ra-226 is present in all uranium minerals and its concentration in uranium ores is about one part radium to three million parts uranium.

Therefore, when uranium ore is solubilized, embedded decay products such as radium are freed from the ore body and also become soluble. Because the radioactive half-life of uranium is very slow, a nearly constant ratio of radium with respect to uranium is found in uranium ore and thus in the groundwater solution formed by the dissolution of uranium ore.

As uranium-containing ore bodies age, the concentration of radium embedded in the ore increases from zero by decay of U-238, but it also decreases due to its own radioactivity. After roughly 20,000 to 30,000 years, the concentration of radium reaches a near-steady state as its rate of formation from uranium is balanced by its rate of disappearance due to its own decay. For several million years after that, the ratio of Ra to U is very close to 3.35×10^{-7} to 1 by weight. Since 1 gram of radium is by definition equivalent to a radioactivity of 1 curie, 3.67×10^{-7} mg of Ra emits 335 pCi of alpha radiation. Accordingly, for every 1 mg/l of uranium liberated from the ore into the groundwater, one would expect to see a related 335 pCi/l of radium.

Given the chemical properties and solubility of uranium, only small amounts of uranium ore such as UO_2 would be soluble in a reducing environment. Uranium would not be liberated into solution until the ore was treated with an oxidation agent, such as being exposed to oxygen gas dissolved in water. Radium (as well as lead and other intermediate-decay species) would mainly be trapped in the ore body occupying the position vacated by the decomposed uranium. It would remain in the ore body and would not be liberated into solution until an oxidation process

dissolves some of the ore orit is physically disrupted by fracturing or grinding. It should be noted that a minute amount of radium could escape the ore body by alpha recoil mechanisms when the radium is formed through radioactive decay (Kraemer and Reid 1984).

IV. The Goliad Uranium Project

A. Proposed Production Site

The Goliad Uranium Project is located in north-central Goliad County, Texas in the Goliad formation. It is not yet under production, but the permitting process is underway. The total project originally consisted of 13 mining leases that cover approximately 1,421 net acres of contiguous properties. The original holder of mining leases was Coastal Uranium. Coastal Uranium conducted an initial exploration project over a very large area that included the current Uranium Energy Corp leases in 1979 and 1980. Moore Energy Corporation acquired the leases to the current property from Coastal Uranium and drilled 479 exploratory holes during 1983 and 1984. Uranium Energy Corp currently holds the leases on a total current mining area of 1140 acres (see Figure 4) and has drilled over 599 confirmation and delineation holes from May 2006 through December 2007. Uranium mineralization, as identified by historic drilling, remains open laterally in all directions, providing expected potential targets for additional drilling and increasing the size of the resource. Uranium deposits were located in four sand aquifers ranging from depths of 90 to 450 feet, showing an average thickness of 14.5 feet and an average ore grade of 0.075 percent across all four sand horizons. The sand layers from shallowest to deepest are designated A, B, C, and D They all are separated by a clay-silt mineral layer of low permeability and were treated by UEC as independent ore bodies (not hydrologically connected).

UEC filed a production area authorization application (PAA-1) with the Texas Commission on Environmental Quality on August 27, 2008, for its first production area. This operation involves mining of the "B-sand" formation as represented in Figures 5 and 6. Figure 5 shows the distribution of various test wells in the 94-acre mine area, as well as the enclosed 36-acre production area. Figure 6 provides the distribution of predicted uranium levels in the B-sand layer. Numbers on the map signify exploratory wells used to establish the uranium level for the area surrounding each individual well.

B. Timeline of Chemical Analyses of Production Zone

In order to establish baseline values for the quality of the groundwater and to determine hydrologic characteristics for the aquifer associated with the B-sand formation, UEC drilled 17 test wells screened to the B-sand layer. These wells are designated as regional baseline (RBLB-1, RBLB-3, RBLB-4, and RBLB-5) and pump test wells (PTW-1 through 13). Ten of these wells were completed before the PAA-1 was submitted. The RBLB wells were completed in May and June of 2007 and the PTW wells 1 through 6 were completed in April of 2008. Results of the first chemical analyses of these wells were reported in PAA-1 to establish baseline values for groundwater quality. PTW wells 7-13 were completed in late July and early August 2008, but were not analyzed until after the filing of PAA-1.

Groundwater from all 13 PTW wells and the four RBLB wells was chemically analyzed three times, although the PAA-1 application only reported the results of the first analyses of PTW wells 1-6 and RBLB wells 1,3,4, and 5. The first tests to establish a groundwater restoration baseline were performed on the RBLB 1 through 4 approximately one to two months after drilling. The first analyses from PTW 1-6 wells were performed in April 2008, immediately after drilling but eight months after the first analyses on the RBLB wells. Of importance is the fact that the pump test in July 2008 took place after the first analyses of PTW 1-6 but before the first analyses of PTW 7-13. The next analytical tests were run on all of the PTW and RBLB wells in July 2009, and the third test on all of the PTW and RBLB wells was conducted in November 2009.

C. Results of Chemical Analyses

The groundwater concentrations of uranium at all test wells determined by the three analyses are represented graphically in Figure 7 and summarized in Table 1. The first data set obtained is shown in Figure 7 and is for the four RBLB wells. Values range from 0.08 mg/l to 0.006 mg/l, averaging 0.052 with a standard deviation of 0.032 (Table 1). These data were obtained in June 2007. Initial tests were then conducted on the PTW wells 1-6 almost a year later in April 2008. Here the values range from 0.059 mg/l to 0.009 mg/l, averaging 0.021 with a standard deviation of 0.021 (Table 1). This second set of data is in general comparable to the earlier values obtained from the RBLB wells. Taking all 10 production zone B wells together, as UEC did in establishing a baseline value in their PAA-1 report to the TCEQ, one finds that 50 percent of them show

uranium concentrations in excess of the EPA's drinking water standard of 0.030 mg/l, and the average value of uranium concentration of 0.032 mg/l for all 10 wells is just over the standard.

Anticipating the addition of eight test wells by July 2008, UEC requested that TCEQ observe the sampling event and collect samples from these additional baseline wells. These wells were tested in July 2008. On March 27, 2009, UEC filed a revised application for production area 1 that included all 18 wells in the baseline determination. Of these wells, 72 percent showed uranium concentrations in excess of the EPA drinking water standard of 0.030 mg/l. The seven additional wells (PTW 7-14) all exhibited uranium concentrations that were significantly higher than those measured in the previous wells (RBLB 1,3,4,5 and PTW 1-6), raising the overall average; thus, the newly reported baseline value for uranium for the groundwater at this mine site increased from 0.052 to 0.115 mg/l.

An inspection of Table 1 shows some very interesting trends. The average value of the uranium concentration in the groundwater for the first measurement on the RBLB wells is 0.052 mg/l, while the average value of the first measurement on PTW 1-6 wells is lower at 0.021 mg/l, yet the newer numbers from PTW 7-14 have an average value that has increased to a much higher value of 0.218 mg/l. A careful look at Figure 7 quickly indicates that combining values from all 18 wells to obtain an average is not good statistics. These data, taken all together, are not random. There is a trend in which uranium levels decrease between the first and second sets of well tests, and then abruptly increase with the third set of wells. These trends indicate that there was a strong perturbation on the formation prior to the first measurement on the RBLB wells that began to relax before the first measurements on the PTW 1-6 wells. This was followed by a second major perturbation before the first measurements on the PTW 7-14 wells.

A consideration of the chemistry of uranium strongly suggests that, before any disturbance of the formation by UEC took place, the uranium existed in an insoluble reduced state, most probably the ore uraninite (UO_2). Through the drilling, casing, screening, and jetting of the test wells—as well as the drilling of the several hundred exploratory wells—oxygen was most certainly introduced into the formation, causing an oxidation and subsequent solution of some of the uranium. This introduction of oxygen contaminated the formation and increased the uranium

concentrations above what would normally be the baseline value. As the oxygen began to be used up by the various minerals present, the formation moved to reestablish a reducing environment, re-reducing the uranium and causing it to partially re-precipitate. But that does not explain the abrupt and major increase in uranium concentrations observed in the first analyses of the PTW 7-14 wells, unless another significant perturbation took place between April 2008, when the groundwater at PTW 1-6 was first tested, and August 2008, when the groundwater at PTW 7-14 was first tested. Such an event clearly did take place. On July 8-9, 2008, pump tests were conducted to establish hydraulic communication between the PTW wells and the baseline monitoring wells BMW 1-22 defining the boundary of the affected ground water area (see Figure 4). Pumping on wells completed in the production zone and measuring the change in the water levels in the boundary monitoring ring wells accomplished this. Two pump tests were conducted serially on PTW-6 and then on PTW-1. Tests lasted for approximately 33 hours each. The total water volume pumped was 75,821 gallons for the PTW-6 test and 73,562 gallons for the PTW-1 test. Normally, there are two phases for each test: water level drawdown during pumping and water level recovery after the pumping, during which 99 percent of the amount of water pumped is returned to the formation. This process will introduce large quantities of oxygenated water, resulting in the elevated values of uranium observed shortly after the pump test by the first chemical analyses performed on wells PTW 7-14 (Figure 7).

This hypothesis can be, and was, tested. After the series of initial tests used to establish a uranium baseline value, two additional chemical analyses were conducted on all 18 test wells. A second chemical analysis was carried out on all 18 wells in July 2009 (15 months after the pump test perturbation), followed by a third analysis in November 2009 (19 months after the pump test perturbation). If additional oxygen was not introduced to the formation and if the formation is naturally in a reduced state, these additional tests will show a slow and steady re-reduction and subsequent re-precipitation and removal of the uranium from the groundwater. In other words, the amount of uranium in the groundwater should exhibit a return to values approaching what it was before the initial disturbance and before any of the testing took place. The reduction reaction may be slow and governed by groundwater movement as well as diffusion. Thus, concentrations may still be approaching the most stable chemical state.

Indeed, the second analysis shows a decrease for every well tested after the pumping test. Without knowing the effect of the pump test on the wells tested before the pump test, one cannot say if they decreased or not. However, since all wells were tested in July 2009, they should all show a decrease in uranium concentration by the time of the third test in November 2009 (four months later). This is truly evident in Figure 7, where the concentrations of uranium from all 18 wells have fallen to low values, averaging 0.005±0.003 mg/l. These concentrations are all well below the EPA requirement and in the range of what would be expected in a reducing environment.

These data taken together clearly show that the baseline value of 0.115 mg/l presented by UEC in its amended PAA-1 is considerably higher than the extrapolated baseline, which now measures to be <0.005 mg/l. The true baseline value for uranium in this formation is very likely less than 0.005 because the re-precipitation is not shown to be complete.

The time series discussed above clearly demonstrates that standard exploratory methods as used by UEC to locate and quantify minable amounts of uranium precipitated in groundwater deposits on the Texas coastal plain are unacceptable. These procedures perturb the formation by the inadvertent introduction of oxygen to such an extent as to invalidate any attempt to establish a real baseline value for uranium. The same may be said for radium, but for other reasons. When uranium ore such as uraninite is dissolved because of the oxidation of the uranium, radium formed by the natural radioactivity of the uranium is released from the ore body. The drinking water standard for the maximum allowable activity of radium is 5 pCi/l (5 picocuries per liter). Table 2 shows that the radium levels measured at all of the RBLB and PTW wells exceed this value by several times. The average level for RBLB wells is 408 pCi/l and for PTW 1-6 it is 138 pCi/l. The average level collected later for the PTW 7-14 is 475 pCi/l. The baseline value of radium reported to the TCEQ by UEC in its amended PAA-1 is the average of all of these wells, or 334 pCi/l with a standard deviation of 426 pCi/l.

How much dissolved radium might be expected in this formation given the amount of dissolved uranium? To a very good approximation, a liter of water containing one milligram of dissolved U(VI) derived from local ore bodies would also contain a proportionate level of solubilized radium. This calculates to be 3.67×10^{-7} mg/l. This amount of radium is equivalent to 335 pCi/l

of Ra per one milligram of uranium. Since the initially measured amounts of uranium range from 0.006 to 0.804 mg/l, predicted amounts of radium should range from 2 to 263 pCi/l. The measured values range from 10 to 1684 pCi/l with an average of 334 (see Table 2). These high measured values of the presence of radium suggest that there is either a source of radium other than that derived from the uranium ore dissolved by the introduction of oxygen by UEC, or that the perturbation on the formation by UEC caused more solution and re-reduction of uranium than was initially measured. The graph of radium concentration vs. time exhibited in Figure 8 shows that the radium concentrations at each of the wells varies by only a small relative amount and may be slightly increasing with time. A comparison of this time trend with that shown by uranium in Figure 8 is consistent with the argument that uranium is being re-precipitated by being reduced through time while radium is not. Further, the slight upward slope in the radium concentration data for each well suggests that some additional uranium may be oxidized, thereby liberating small additional amounts of radium, during the approximately two-and-a-half-year time period of the measurements.

Unfortunately, one cannot calculate an exact amount of expected radium in terms of pCi/l that is a true baseline level of radium at the Goliad site, but it can be expected that without any liberation of radium from the uranium ore by means of exploration activity, the concentrations would likely be very low. It is highly possible that true baseline levels for radium concentration are below the EPA drinking water standard of 5 pCi/l.

All of the data used in the analysis described in this section were obtained by Uranium Energy Corporation. Primary source data obtained before August 2008 can be found as public information in the UEC application to the TCEQ for a Goliad project production area authorization (PAA-1, August 27, 2008). Additional data are also available in an addendum filed with the TCEQ on March 27, 2009. Further data not appearing in either section of the PAA-1 are held through disclosure by the law firm of Blackburn & Carter, Houston, Texas.

V. Additional Considerations Relating to Other Similar Mines

A. Groundwater Restoration After Mining

Although the primary focus of this paper addresses problems associated with baseline concentrations of uranium and radium in uranium ISL mines, it must be pointed out that groundwater restoration to baseline values at ISL mines after the recovery phase is just as problematic. The greatest number of uranium in-situ leaching mines occurs in Texas. As pointed out above, the most complete analysis of baseline recovery in Texas mines was reported by Susan Hall (2009) for the U.S. Geological Survey. She found consistently high restoration values as well high baseline values. All PAAs in her study received amended restoration goals increasing the restoration concentration for at least one element after operators, employing a reasonable degree of restorative effort, could not restore the groundwater to baseline values. At the time these data were analyzed, only 22 PAAs from 13 mines were available.

Baseline standards for all 77 Texas PAAs are used to characterize Texas ISL wells. Because of concentration values consistently higher than those defining potable drinking water, the argument was commonly made that before mining, groundwater in ISRL well fields is so contaminated it could not be used for human consumption because one or more chemicals had a concentration higher than the MCL set by the U.S. Environmental Protection Agency. All PAAs contained radium levels above the MCL, and 95 percent contained uranium levels above the MCL. Thus, before mining, associated aquifers were typically granted exemptions (or "aquifier exemptions") from the Clean Water Act by the EPA. Therefore, the TCEQ was not particularly concerned with post-restoration concentration values that were above the MCL or recommended standards. In fact, 86 percent of the PAAs reported uranium concentrations and 100 percent reported radium concentrations in restoration water that were above the MCL or recommended standards.

Since the recommended procedure for obtaining measured baseline concentrations is flawed, causing the resulting baseline concentrations for uranium and radium to be elevated above the undisturbed concentrations, I call into question the granting of any aquifer exemptions from the Clean Water Act. Furthermore, since post-restoration concentrations for radium and

uranium are also generally high, the whole mining process should be closely examined and modified, or disallowed.

B. Permanent Condition of Mining Site

I have shown above from actual baseline data that re-precipitation of uranium will return groundwater back to more accurate readings of real quality, given sufficient time. Why, then, will full-scale mining permanently degrade the aquifer? The answer is two-fold. Firstly, the radium is not re-precipitated by a reducing environment. A reducing environment does not affect its levels. Radium will be elevated by the initial solution of the uranium ore and will thus stay elevated unless fully removed by the mining and restoration process. This evidently does not happen since, in Texas, 100 percent of the restored mines reported high radium concentrations. Secondly, restoration values of uranium in Texas mines are elevated above MCL or recommended standards 86 percent of the time. The mining process is one of oxidation, not only of uranium but also of the surrounding matrix. If after mining is completed, the mining process itself has removed the reducing environment, there is no mechanism in place to re-precipitate the uranium. Again, the restoration procedure appears to be flawed.

C. Can ISL Mining of Uranium Be Made Safe for Groundwater?

The question that now remains is, if the process for ISL mining is flawed, what, if anything, can be done to correct it? With respect to baseline measurements of uranium and radium, the general answer is simple. Namely, assure that the ambient reducing conditions that originally precipitated the uranium ore remain unchanged during baseline concentration determinations. Specifically what to do is more complex. Oxygen is introduced into the ore formation mainly by the water used during drilling, casing, screening, and washing a baseline test well. A newly designed microprobe that could be inserted into the formation without introducing water or even air might be constructed. Perhaps a very small diameter drill using a nonaqueous drilling medium could be employed that would house a small groundwater sampler. An alternative solution could be to de-oxygenate the water used in creating the test well. One might not want to use an antioxidant or a reducing agent because that would decrease the concentration of any uranium that might be originally present. Elevated post-restoration concentrations of uranium might be lowered if a way were found to return the reduction potential to near or below its original value.

VI. Conclusions

I conclude that, because of a flawed recommended drilling procedure, oxidation of uranium ore bodies regularly occurs during baseline concentration measurements to obtain a mining permit. Introduced oxygen causes uranium ore to dissolve, thereby artificially elevating concentrations of uranium in water samples from the test well locations. The process of dissolving uranium also liberates radium that would otherwise remain in the intact ore body.

In my opinion, normally acquired test well data do not accurately measure a baseline level of uranium and radium in the aquifers under the test site. There is a high probability that the test well water is contaminated with a concentration of uranium higher than the true baseline value due to the presence of oxygen in the test well and subsequent reactions. It is simply inappropriate to disrupt the system in order to obtain baseline data.

It is my conclusion that issuing either the in-situ application or the PAA-1 application, where existing protocol is used, is not in the public's interest. Prior to exploration activities, the water within the proposed production zone might possibly be of drinking water quality. Issuing either permit on the basis of falsely elevated baseline concentrations of uranium and radium would exempt a possible source of drinking water and would preclude use of this water indefinitely.

I believe that better and less invasive methods can be developed that will ensure accurate baseline values of uranium and radium concentrations in the groundwater of the ore-body containing aquifer.

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Figure 1. Location of uranium deposits in Texas

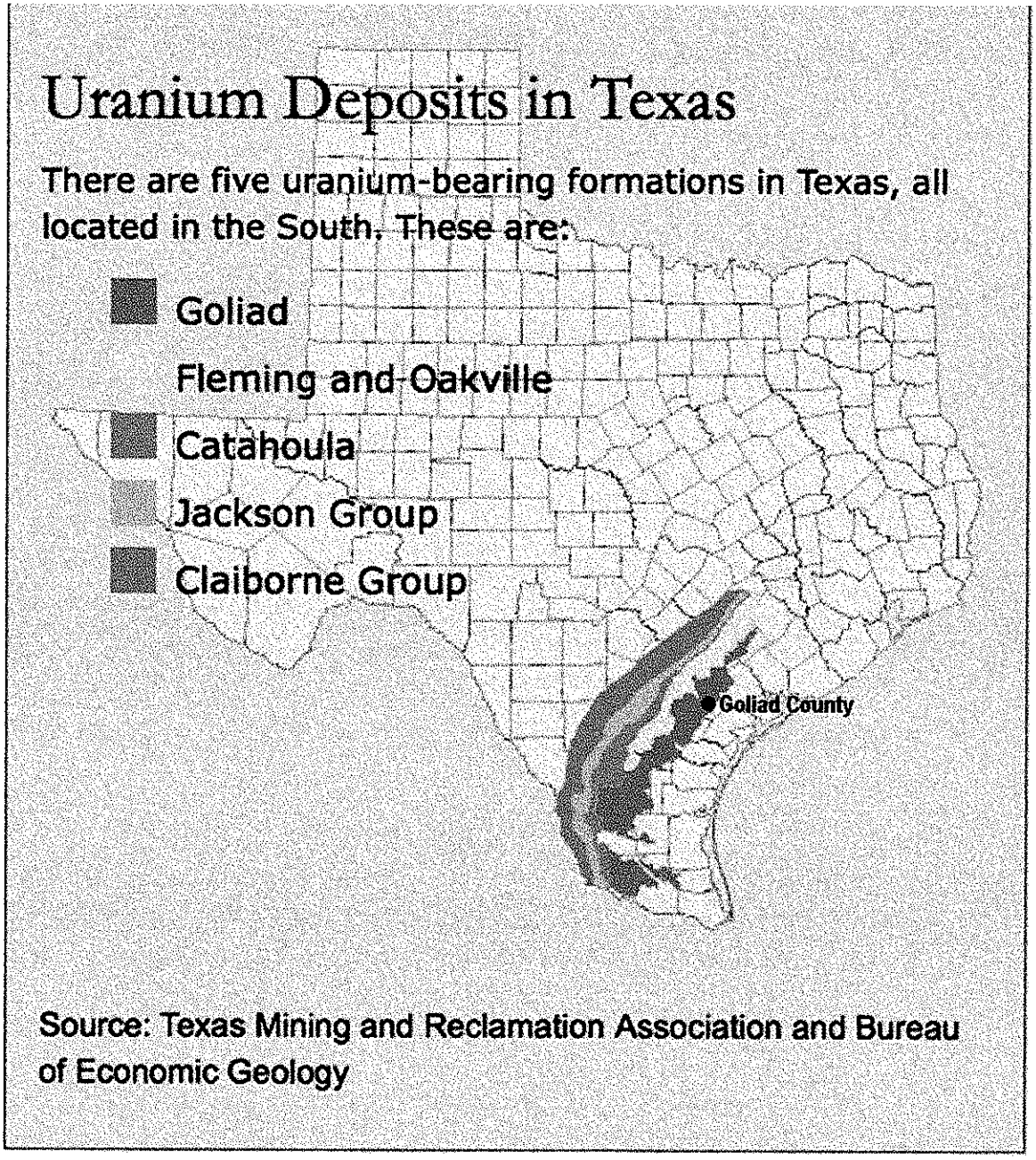

Figure 2. Radioactive decomposition chain for U-238 to lead-206

[illegible]	[illegible]	[illegible]
	URANIUM-238	4.5×10^9 years
a	THORIUM-234	24.5 days
b	PROTACTINIUM-234	1.14 minutes
b	URANIUM-234	2.33×10^5 years
a	THORIUM-230	8.3×10^4 years
a	RADIUM-226	1590 years
a	RADON-222	3.825 days
a	POLONIUM-218	3.05 minutes
a	LEAD-214	26.8 minutes
b	BISMUTH-214	19.7 minutes
b	POLONIUM-214	1.5×10^{-4} seconds
a	LEAD-210	22 years
b	BISMUTH-210	5 days
b	POLONIUM-210	140 days
a	LEAD-206	stable

Figure 3. Phase diagram showing Eh and Ph dependence in a carbonate system on stability in water solutions of uranium compounds of the two different oxidation states U(IV) and U(VI).

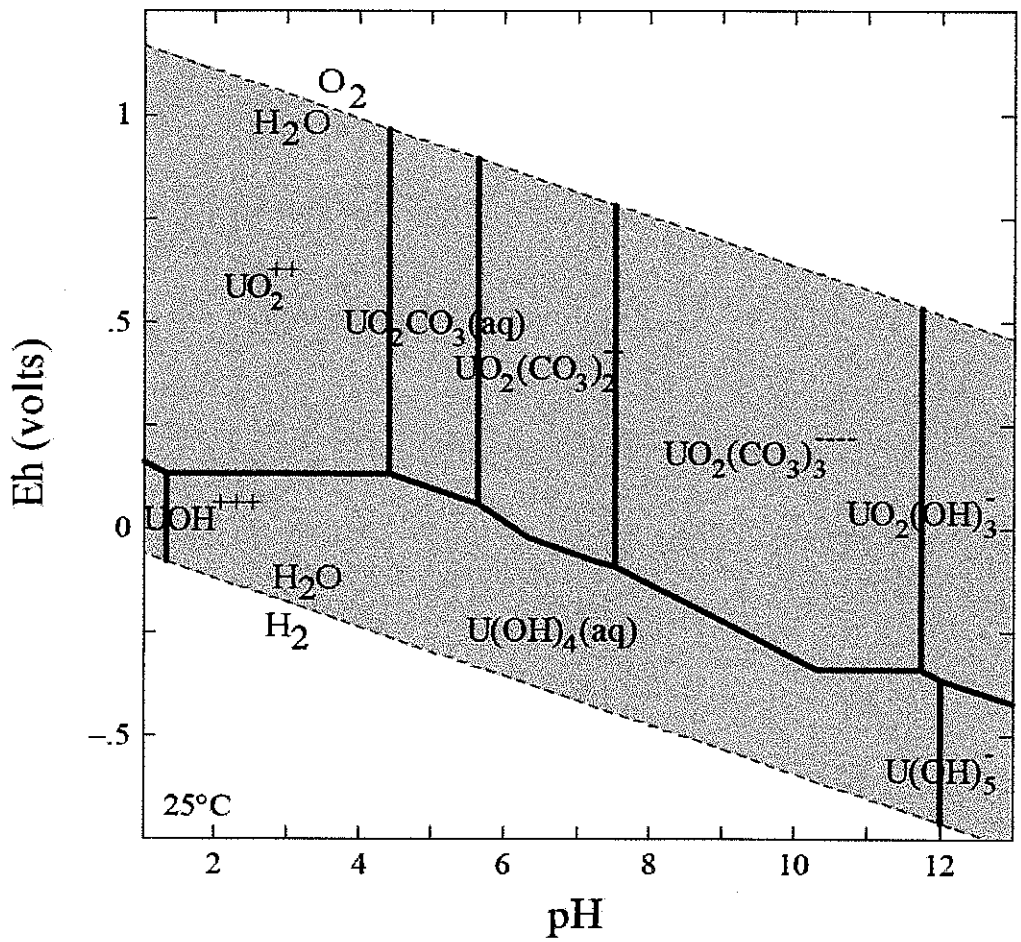

Figure 4. Permit map showing NW and SE faults, aquifer exemption boundary, locations of the four sand formations, and proposed mine and production areas. (Source: UEC)

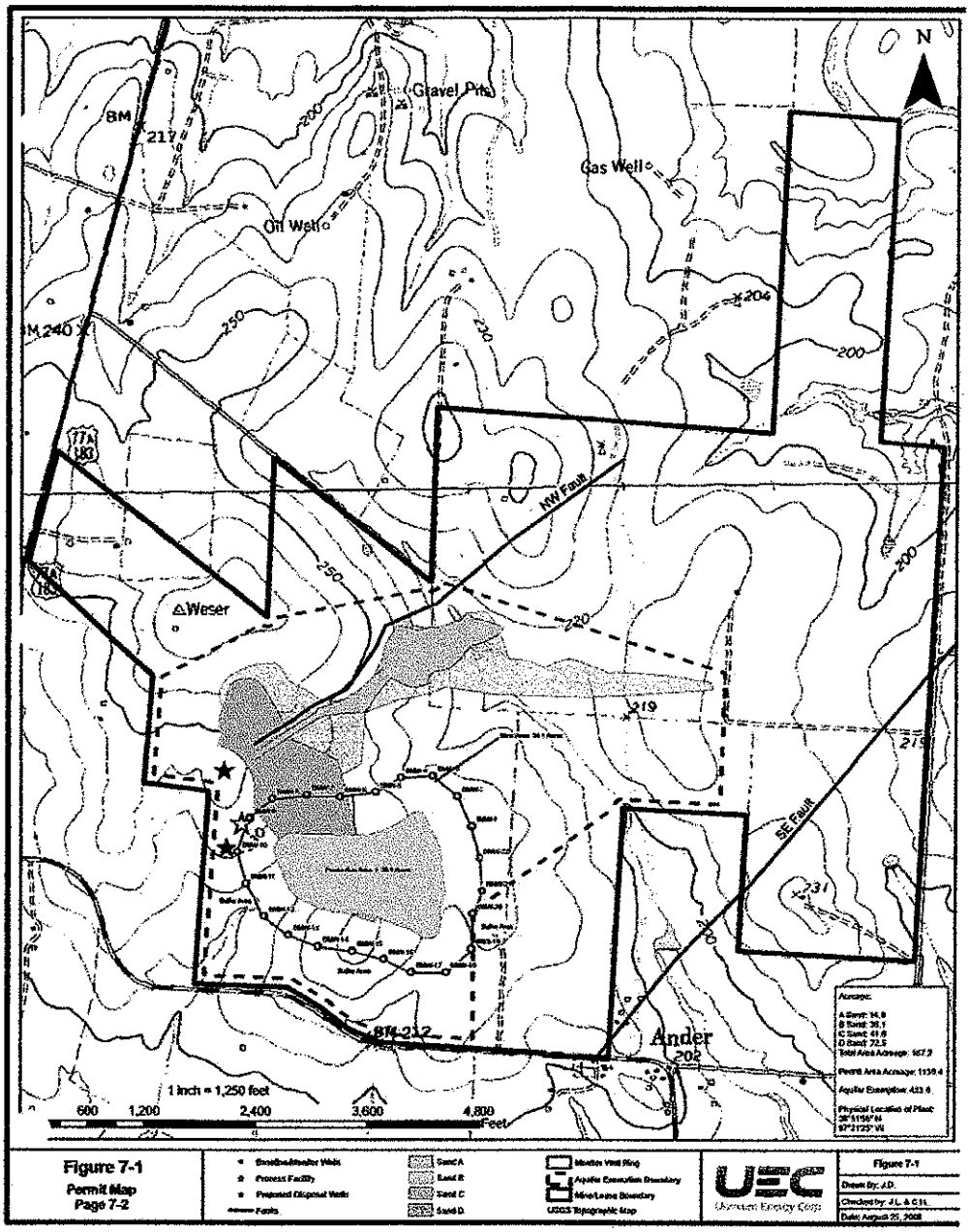

Figure 5. Distribution of the various test wells in the 94-acre mine area as well as the enclosed 36-acre production area. All wells used to obtain baseline chemical data are located in the production area. (Source: UEC).

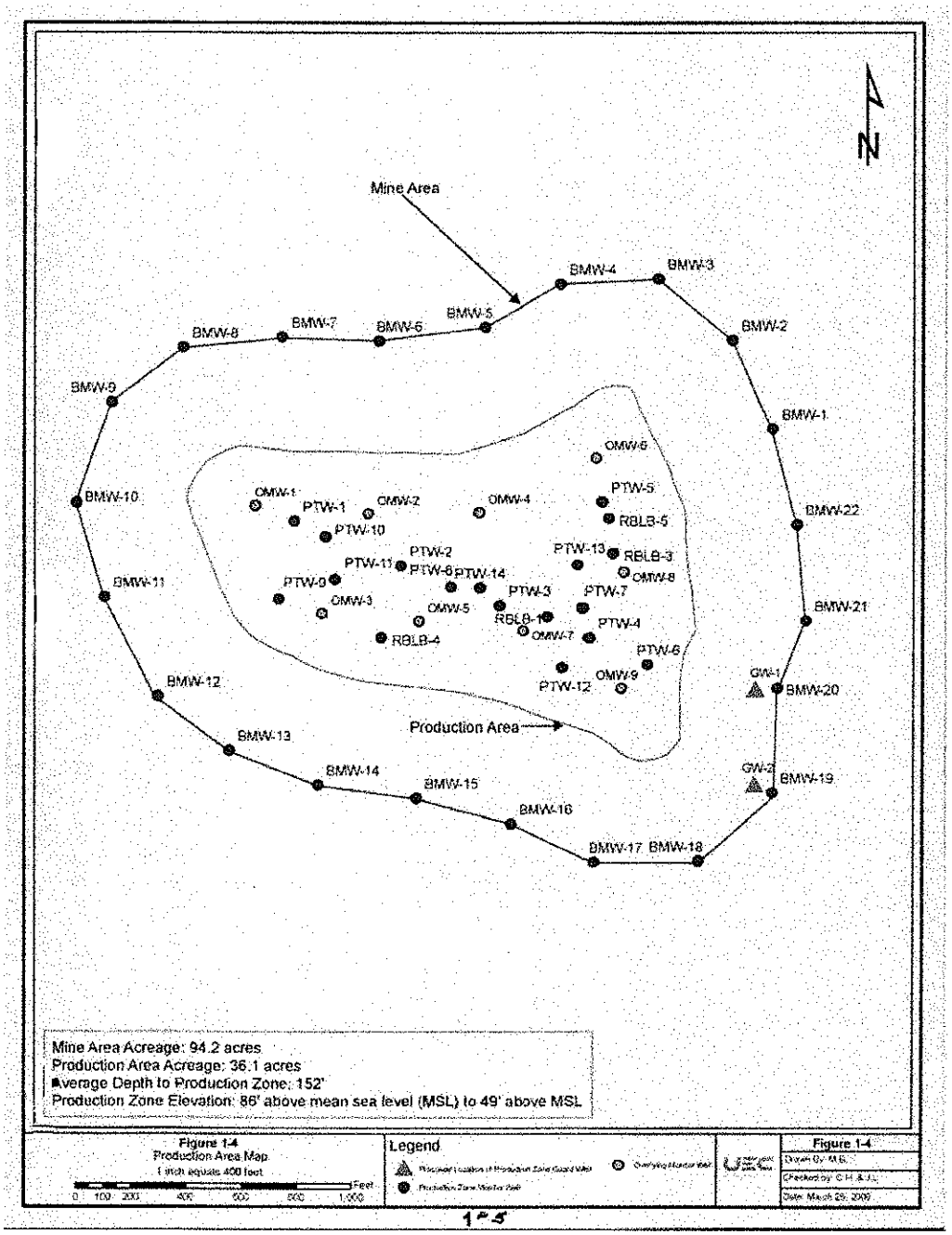

Figure 6. Distribution of predicted uranium levels in the B-sand layer

Numbers on the map signify exploratory wells used to establish the uranium level for the area surrounding each individual well. (Source: UEC)

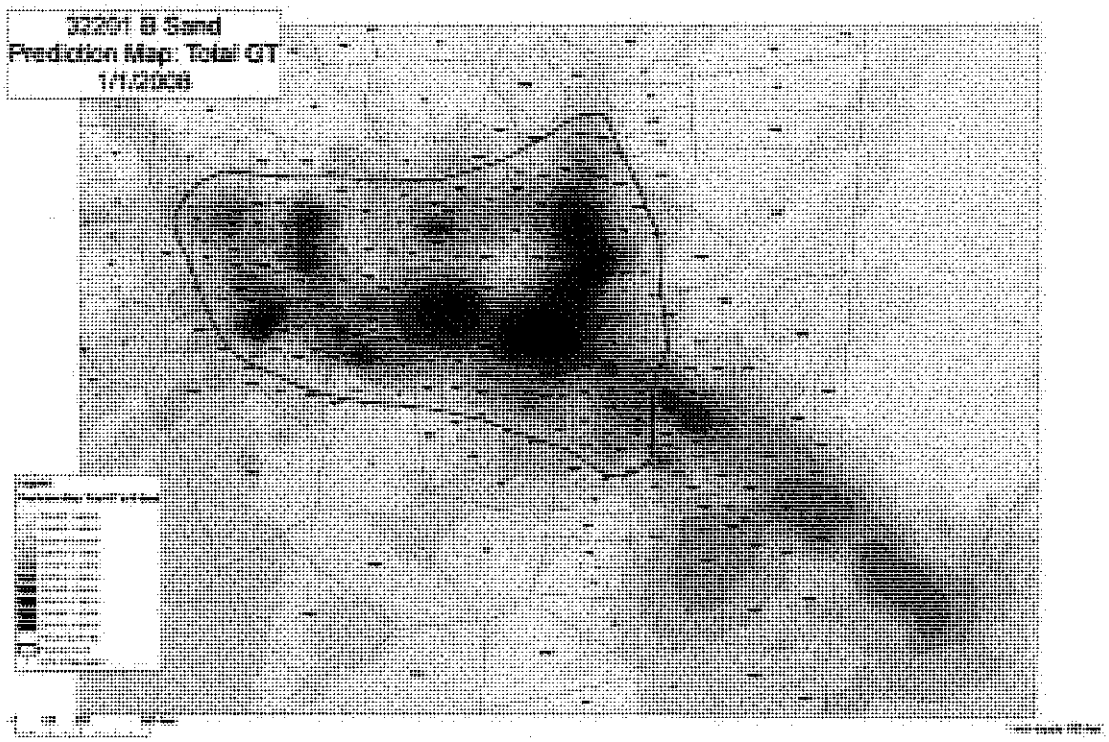

Figure 7. Time plot of the test values of uranium for the three sampling dates for each of the PTW and RBLB wells.

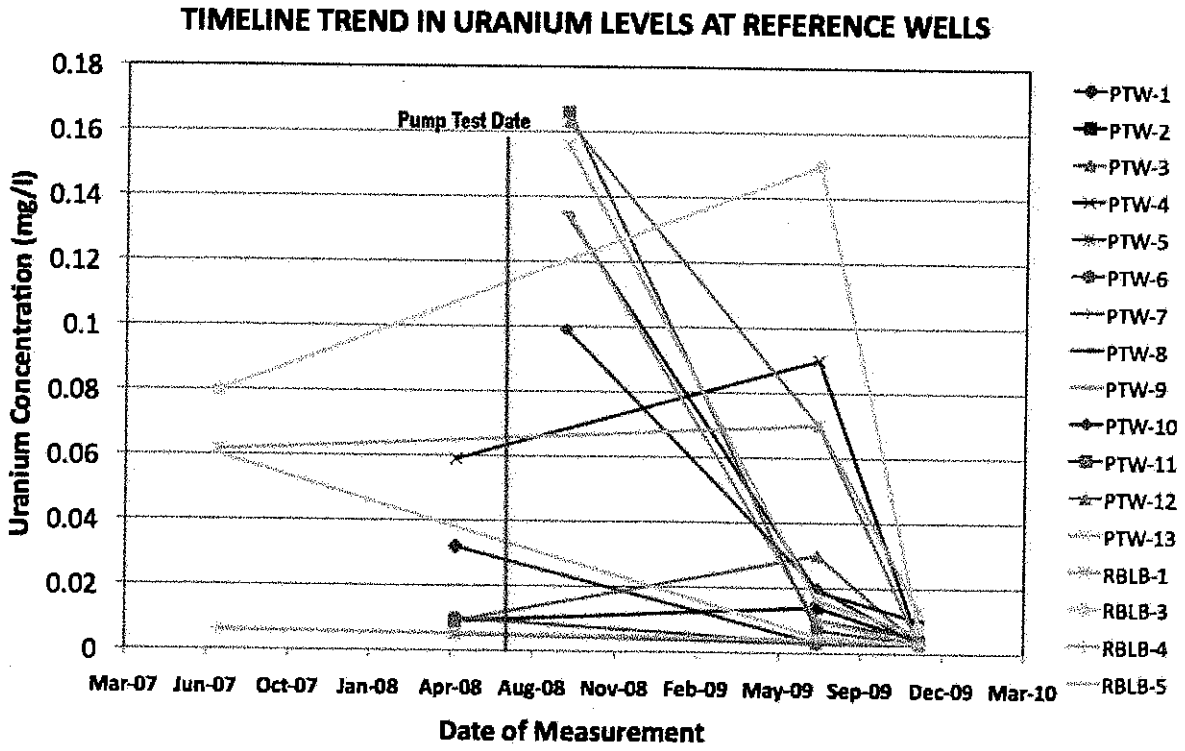

Figure 8. Time plot of the test values of radium for the three sampling dates for each of the PTW and RBLB wells.

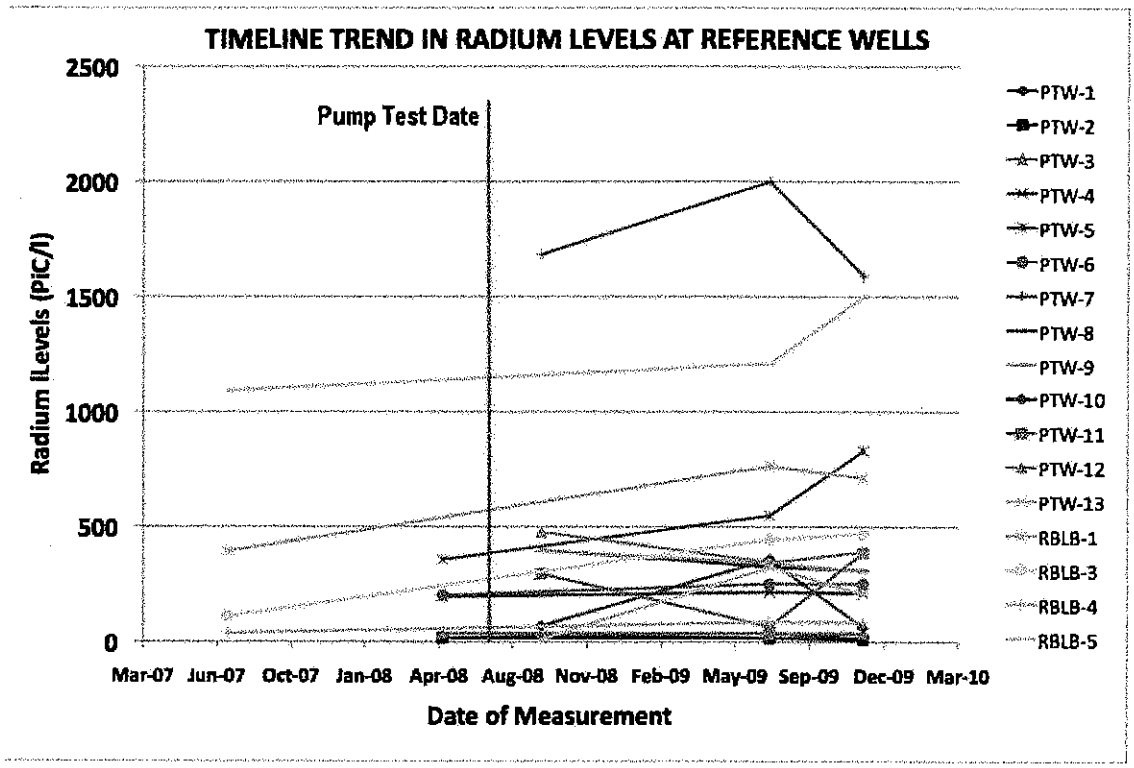

Table 1. Uranium concentrations of all test wells from all analyses

Test	Uranium	RBLB 1,3,4,5 (mg/l)	PTW 1-6 (mg/l)	PTW 7-14 (mg/l)	ALL WELLS (mg/l)
First Test	Average	0.052	0.021	0.218	0.115
	High	0.080	0.059	0.804	0.804
	Low	0.006	0.009	0.099	0.006
	Stand. Dev.	0.032	0.021	0.239	0.161
Second Test	Average	0.057	0.024	0.020	0.029
	High	0.150	0.090	0.019	0.150
	Low	0.004	0.003	0.005	0.003
	Stand. Dev.	0.069	0.034	0.021	0.040
Third Test	Average	0.007	0.003	0.005	0.005
	High	0.013	0.004	0.010	0.013
	Low	0.003	0.003	0.003	0.003
	Stand. Dev.	0.004	0.003	0.003	0.003