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resources &amp; energy

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Proj. No.:  
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**RE: RESPONSE TO NDEQ EXCURSION MONITORING ISSUES**

Mr. Moody:

This letter report provides a response to Nebraska Department of Environmental Quality concerns regarding excursion monitoring at the Crow Butte Resources (CBR) uranium ISR facility.

**BACKGROUND**

At CBR, monitoring wells surrounding the production areas are sampled on a biweekly basis. These groundwater samples are analyzed for the indicator parameters conductivity, alkalinity and chloride. These indicator parameters were selected and included in CBR site license conditions because these constituents are present in the production fluid at higher concentrations than in the pre-mining groundwater and are transported in groundwater at a much higher rate than other constituents in the production fluid, such as uranium. Chemical parameters such as uranium move at a much slower rate than indicator parameters because uranium is slowed by physical and chemical process in the aquifer including adsorption onto mineral surfaces and chemical reactions (e.g. oxidation/reduction). These processes do not affect excursion indicator parameters, which move at the same speed as groundwater (e.g. "conservative" chemical parameters). Consequently, detection of increasing concentrations of indicator parameters provides the earliest possible warning of an excursion.

An excursion generally occurs when the rate of injection exceeds the rate of groundwater extraction ("over-injection") within a portion of an actively mined wellfield for a period of time. An excursion normally occurs locally over a small portion of the mine unit, usually on the scale of a few mine patterns or well house.

If an excursion is confirmed at a monitoring well, CBR responds immediately by curtailing injection and increasing the extraction rate from perimeter production mining wells (corrective action). The corrective action pumping lowers the water level in the area where the excursion originated and causes groundwater to flow back toward the active mining area until the excursion



is fully recovered. The corrective action is considered complete and the well is removed from excursion status when groundwater quality has been restored to the quality observed prior to the excursion (e.g. indicator parameters below lower control limits) and stability has been demonstrated for a period of six (6) consecutive weeks.

***Issue 1 - When Upper Control Limits (UCL's) are exceeded in a monitoring well, how far beyond the monitoring well do the constituents travel before the corrective action captures them?***

An analysis of the rate of groundwater movement (based on actual CBR excursion data) clearly demonstrates that CBR's excursion monitoring program is adequate and that additional monitoring wells or increased sampling frequency are unnecessary.

In order to determine how far chemical constituents migrate during an excursion event, it is necessary to determine the rate at which groundwater and conservative chemical parameters are moving. To accomplish this task, the excursion observed in May 2008 in Mine Unit 9 (MU9) at CBR will serve as a model. The resulting rate of groundwater movement will demonstrate that CBR's current excursion monitoring program is adequate and that additional monitoring wells or increased sampling frequency is unnecessary.

**ADEQUACY OF EXISTING EXCURSION MONITORING PROGRAM**

At CBR, uranium is recovered from groundwater extracted from the Basal Chadron Sandstone. Studies of groundwater flow at CBR indicate groundwater within the mined aquifer moves very slowly, at a rate of approximately 5 to 10 feet per year under natural (e.g. non-pumping) conditions<sup>1</sup>. Locally, groundwater velocity may increase due to stresses imposed on the aquifer, including pumping and injection of groundwater conducted as part of CBR mining operations.

In the case of the May 2008 excursion in MU9, water balance data collected from Well Houses 45 and 47 (WH45/47) indicates that a local over-injection of mining solutions began in the first week of January 2008 and continued sporadically thorough the end of April 2008 (Figure 1). The average rate of over-injection in WH45/47 during this period was approximately 12 gallons per minute (gpm). The onset of the excursion was reflected as a rise in water level in the adjacent monitoring well ring during this time, including excursion monitoring wells CM9-3 and CM9-5 (Figures 2 through 10).

On May 15, 2008, monitoring well CM9-5 was placed on excursion status following repeated observations of increasing chloride, alkalinity, and conductivity above control limits. Similarly, well CM9-3 was placed on excursion status two weeks later, on May 30, 2008. Given the location of CM9-3 and CM9-5 downgradient of WH45/47, it can be concluded that the May 2008 excursion event was the result of a local over-injection which began approximately 18 weeks earlier, as illustrated by the arrival of the chloride plume in CM9-3 in May 2008 (Figure 1). Given knowledge of the duration of the over-injection and the distance between the mine patterns and monitoring

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<sup>1</sup> USNRC Source Material License SUA-1534 Renewal Application, Crow Butte License Area, November 2007



wells CM9-3 and CM9-5, the time of travel and the velocity of conservative chemical movement during the May 2008 excursion event can be calculated.

In this calculation, it is assumed a starting date for the excursion of January 1, 2008 corresponds to the onset of a local over-injection in WH45/47. For CM9-3, an excursion arrival date of May 15, 2008 is assumed based on the first noticeable increase in chloride, alkalinity and conductivity at this location (Figure 1). The resulting time of travel for conservative chemical parameters is 135 days. Given a distance of 270 feet from the mine patterns to monitoring well CM9-3, the groundwater velocity and speed of conservative chemical movement during the excursion is estimated to be 2.0 ft/day. A similar analysis for well CM9-5 using a distance of 250 feet from the mine patterns to the monitoring well yields a groundwater velocity of 1.85 ft/day. The resulting groundwater velocities calculated for CM9-3 and CM9-5 are very similar.

Based on a maximum calculated groundwater velocity of 2.0 ft/day, conservative chemical parameters will not move more than 14 feet beyond the monitoring well ring once weekly sampling is initiated and/or control limits have been exceeded. This analysis is conservative, because the speed of movement in the vicinity of the monitoring well ring is actually lower than the average velocity computed herein. This is due to the fact that groundwater velocity is greatest near the source (injection well) and decreases rapidly with increasing distance from the source of over-injection (e.g. monitoring well ring).

As discussed in our response to Question #2, non-conservative parameters such as dissolved uranium would move a much shorter distance during an excursion and would never be detected in monitoring wells. Under the conditions encountered at CBR, the total distance uranium could be expected to travel would be 0.5 to 15% of the distance traveled by a conservative parameter such as chloride, or less than 40 feet beyond the active mining area.

#### **ADEQUACY OF EXISTING EXCURSION CORRECTIVE ACTION PROGRAM**

In response to the May 2008 excursion event, CBR began excursion corrective action by curtailing injection and increasing the extraction rate from perimeter production mining wells in WH45/47. Excursion corrective action was initiated immediately on May 15, 2008 as shown in Figure 1.

During the corrective action phase, water levels in CM9-3 and CM9-5 were observed to decrease by more than 20 feet compared to an increase of less than 15 feet during the excursion phase, which indicates that corrective action pumping affected a significantly larger area than the over-injection that created the excursion (as desired). Further, the excursion corrective action pumping rate in WH45/47 varied from approximately 20 to more than 80 gpm (Figure 1), a significantly higher rate than the over-injection that caused the excursion. Because groundwater velocity (and speed of chemical movement) is directly proportional to the pumping or injection rate, it can be concluded that the excursion plume was recovered and remediated in significantly less time than the 18 weeks required for the excursion to migrate to the monitoring well ring. Monitoring well sampling data from CM9-3 and CM9-5 (Figures 2 through 10) confirm that groundwater quality had returned to baseline (pre-excursion) conditions within three weeks of onset of corrective action. Based on these data and calculations, the CBR excursion corrective



action program is more than adequate to accomplish full restoration of groundwater quality within the area impacted by the excursion in a timely fashion.

**Issue 2: *Could production fluids from the excursion detected in Mine Unit 9 in May 2008 and June 2009 increase uranium concentrations?***

Production fluids from excursions would not increase uranium concentrations at the monitoring well locations because the rate of uranium groundwater transport is much lower than the transport rate for the indicator parameters. The movement of dissolved uranium is slowed significantly by physical and chemical process in the aquifer including adsorption onto mineral surfaces and chemical reactions (e.g. oxidation/reduction).

Lower control limits and upper control limits were established for excursion indicator parameters using the groundwater concentrations measured at the monitoring wells before uranium ISR began (Tables 1 through 3). During uranium production, groundwater at the monitoring wells is sampled every two weeks and analyzed for the indicator parameters. If two or more indicator parameters exceed their lower control limits at a monitoring well or one parameter exceeds its upper control limit, a second groundwater sample is collected within 48 hours of the first sample to confirm that an excursion has occurred.

Excursions were detected at wells CM9-3 and CM9-5 in May 2008 and during a separate excursion at well CM9-4 in June 2009. Indicator parameter data for these monitoring wells are provided in Tables 1 through 3 along with available uranium concentrations and pH data. The data demonstrate that the excursions were resolved quickly, with the indicator parameter concentrations returned to less than the lower control limits shortly after the excursions began. Uranium concentrations measured in samples from wells CM9-3 and CM9-5 after the May 2008 excursion (e.g. August 2008 and September 2008) remained consistent with pre-excursion concentrations and are significantly below the uranium groundwater restoration standard (Tables 1 and 3).

Uranium concentrations did not increase at the monitoring wells during or after the excursions because uranium is transported through the aquifer at a much slower rate than indicator parameters, and all water is returned to the active mining pattern area during the abatement of any excursions that occur. The different rates at which constituents are transported through an aquifer can be calculated using their respective distribution coefficient ( $K_d$ ) values. The  $K_d$  value is defined as the ratio of the constituent concentration associated with the solid phases in the aquifer and the concentration of the constituent in the groundwater:

$$K_d = \frac{\text{concentration of constituent in the solid phase}}{\text{constituent concentration in solution}} \quad (1)$$

A high  $K_d$  ( $> 10$  ml/g) indicates that a constituent is strongly retained by the aquifer solids and will travel much more slowly than the average groundwater velocity. Even a constituent with a relatively small  $K_d$  (e.g., equal to 1 ml/g) will be transported through groundwater much more slowly than a constituent that is not retained by the solid phases ( $K_d$  equal to 0 ml/g), as illustrated by Figure 11.



The  $K_d$  value is used to calculate the retardation factor ( $R_d$ ) for use in groundwater transport calculations. The  $R_d$  is the velocity of a constituent relative to the average linear velocity ( $v$ ) of the groundwater. The  $R_d$  for a constituent is described by the equation:

**Table 1. Monitoring well CM9-3 data before, during and after excursion**

Date	pH	Alkalinity (mg/L)	Chloride (mg/L)	Conductivity (µmhos/cm)	Uranium (mg/L)
3/27/2003	7.95	311	174	--	0.0303
5/1/2008	--	310	198	1,920	--
5/15/2008	--	333	215	2,010	--
<b>5/30/2008<sup>a</sup></b>	--	<b>374</b>	<b>227</b>	2,180	--
<b>5/31/2008</b>	--	<b>393</b>	<b>236</b>	<b>2,220</b>	--
6/10/2008	--	339	215	2,040	--
6/17/2008	--	317	207	1,950	--
6/24/2008	--	312	197	1,930	--
7/1/2008	--	303	197	1,890	--
7/8/2008	--	306	192	1,890	--
7/15/2008	--	301	194	1,880	--
7/24/2008	--	302	188	1,860	--
8/7/2008	--	300	191	1,860	--
8/21/2008	7.90	298	181	--	0.0167
9/5/2008	7.95	292	202	--	0.0145
Lower Control Limit		372	222	2,200	--
Upper Control Limit		440	266	2,664	--
Restoration Standard					5

a – bold text indicates excursion dates and parameters exceeding lower control limits

**Table 2. Monitoring well CM9-4 data before, during and after excursion**

Date	pH	Alkalinity (mg/L)	Chloride (mg/L)	Conductivity (µmhos/cm)	Uranium (mg/L)
8/21/2008	7.91	298	207	--	0.0189
9/5/2008	8.00	292	202	--	0.0139
4/30/2009	--	382	230	2,230	--
5/14/2009	--	<b>395<sup>a</sup></b>	236	2,250	--
<b>5/29/2009</b>	--	<b>492<sup>b</sup></b>	279	<b>2,650</b>	--
<b>6/12/2009</b>	--	<b>472<sup>b</sup></b>	269	2,540	--
6/16/2009	--	<b>458</b>	269	2,520	--
6/23/2009	--	<b>450</b>	259	2,520	--
6/30/2009	--	<b>457</b>	266	2,530	--
7/7/2009	--	<b>444</b>	260	2,480	--



7/14/2009	--	<b>429</b>	254	2,430	--
7/21/2009	--	<b>419</b>	250	2,410	--
7/23/2009	--	<b>422</b>	250	2,400	--
8/6/2009	--	<b>405</b>	237	2,330	--
8/20/2009	--	<b>399</b>	232	2,300	--
9/3/200	--	385	231	2,270	--
Lower Control Limit		386	319	2,556	
Upper Control Limit		464	383	3,067	--
Restoration Standard					5

a – bold text indicates excursion dates and parameters exceeding lower control limits

b – alkalinity exceeded upper control limits on 5/29/2009 and 6/12/2009

**Table 3. Monitoring well CM9-5 data before, during and after excursion**

Date	pH	Alkalinity (mg/L)	Chloride (mg/L)	Conductivity (µmhos/cm)	Uranium (mg/L)
3/27/2003	8.40	312	228	--	0.0186
4/17/2008	--	329	212	2,010	--
5/1/2008	--	<b>423<sup>a</sup></b>	245	2,350	--
<b>5/15/2008</b>	--	<b>469<sup>b</sup></b>	259	<b>2,500</b>	--
<b>5/16/2008</b>	--	<b>456<sup>b</sup></b>	260	<b>2,470</b>	--
5/20/2008	--	<b>394</b>	234	2,250	--
5/27/2008	--	338	214	2,040	--
6/3/2008	--	323	209	1,960	--
6/10/2008	--	329	210	2,000	--
6/17/2008	--	330	211	2,010	--
6/24/2008	--	350	217	2,070	--
7/8/2008	--	328	204	1,980	--
7/10/2008	--	325	202	1,960	--
7/24/2008	--	325	206	1,970	--
8/7/2008	--	326	209	1,980	--
8/21/2008	7.91	320	194	--	0.0230
9/5/2008	7.98	297	187	--	0.0103
Lower Control Limit		374	274	2,460	--
Upper Control Limit		449	320	2,952	--
Restoration Standard					5

a – bold text indicates excursion dates and parameters exceeding lower control limits

b – alkalinity exceeded upper control limit on 5/15/2009 and 5/16/2009



$$R_d = \frac{v}{v_c} = 1 + \frac{\rho_b}{n} (K_d) \quad (2)$$

$v_c$  is the linear velocity of the point in a plume at which the concentration ratio  $C/C_0 = 0.5$ , with  $C_0$  equal to the initial concentration,  $\rho_b$  equal to the bulk density, and  $n$  is porosity.

Site-specific values are known for the bulk mass density ( $1.80 \text{ g/cm}^3$ ) and aquifer porosity (0.29) at CBR, so the  $K_d$  values for different constituents are the only additional parameters that must be determined to calculate constituent transport. Using the site-specific values for bulk mass density and porosity, equation (2) at the CBR site can be simplified to:

$$R_d = 1 + 6.2 (K_d) \quad (3)$$

If a constituent does not associate with the solid phase through precipitation or sorption, its  $K_d$  is 0 ml/g and the constituent moves at the same speed of groundwater ( $R_d = 1$ ). Because chloride solid phases are extremely soluble and chloride is negligibly sorbed by aquifer solids, chloride has a  $K_d$  equal to 0 ml/g and an  $R_d = 1$  for groundwater transport at the CBR site. Consequently, chloride is among the first constituents to arrive at a monitoring well during an excursion. Because alkalinity is mainly composed of carbonate ions that would be poorly attenuated at the site and conductivity depends on the total dissolved ions in solution, these parameters also behave conservatively and in a manner similar to chloride. This effect can be seen in the monitored alkalinity, chloride and conductivity data for wells CM9-3, CM9-4 and CM9-5 (Figures 2 through 10), which show that these three parameters simultaneously increased during the excursions.

Transport calculations that demonstrate the relative rate of uranium movement at the CBR site during an excursion require the selection of a  $K_d$  value consistent with site aquifer chemical conditions. Unlike chloride, uranium at the CBR site has a  $K_d$  greater than zero because chemical processes in the aquifer cause uranium to be retained by the mined formation solids. Uranium mobility is strongly affected by whether aquifer conditions are oxidizing or reducing, by the solid phases present in the aquifer and by the groundwater composition, particularly pH and carbonate concentrations (EPA 1999, Vandenhove et al. 2007, Vandenhove et al. 2009).

The production-zone groundwater is oxidizing, with carbonate concentrations that have been increased to enhance uranium mobility for the purpose of uranium recovery. Uranium in the production fluid is present as uranium (VI) and the groundwater pH is approximately 8 (Tables 1 through 3). The mined formation solids at the CBR site include quartz, clays, feldspar and abundant reducing materials in the form of pyrite [ $\text{FeS}_2(\text{s})$ ] and organic carbon (Stewart 2002). The formation solids in oxidized portions of the aquifer also contain iron oxides and hydroxides produced by pyrite oxidation. These solids will reduce uranium mobility as it migrates away from the production zone.

The formation at the CBR site contains abundant reducing materials in the form of pyrite [ $\text{FeS}_2(\text{s})$ ] and organic carbon (Stewart 2002). Reduction of oxidized uranium(VI) to uranium(IV) by pyrite and reduction by organic carbon in the formation are expected to limit uranium mobility at the CBR site and contribute to a higher  $K_d$ .





Uranium that remains in the uranium(VI) oxidation state at CBR is likely to be sorbed by clays, organic carbon and iron oxides and hydroxides (EPA 1999, Vanderhove et al. 2007), increasing the uranium  $K_d$ . Groundwater pH has a significant effect on uranium(VI) sorption to solids, with maximum amounts of uranium(VI) sorption observed from pH 5 to 7. The presence of elevated groundwater carbonate concentrations can limit uranium(VI) sorption (EPA 1999, Vandenhove et al. 2007, Vandenhove et al. 2009) although uranium(VI) reduction can still occur in the presence of carbonate (Regensburg et al. 2009).

Vandenhove et al. (2009) compiled uranium  $K_d$  values from the literature and statistically evaluated the data based on sand and clay contents, organic matter content and pH. Statistical evaluation of 178 uranium  $K_d$  values indicated that textural classification had little effect on  $K_d$ , but that pH significantly affected  $K_d$  values. Vandenhove et al. (2009) determined that the regression equation:

$$\log K_d = -0.77 \times \text{pH} + 7.7 \quad (4)$$

described the relationship between uranium  $K_d$  and pH for solutions with pH values ranging from 5.5 to 8.8. Equation (4) yields a predicted  $K_d$  of 35 ml/g for CBR groundwater with a pH of 8. This  $K_d$  value represents a best estimate of uranium transport as groundwater flows away from the production zone and encounters reducing phases such as pyrite and organic carbon as well as iron oxides and hydroxides and clays likely to sorb uranium from solution. Using the best-estimate  $K_d$  of 35, the best-estimate  $R_d$  calculated using equation (3) is 218. This  $R_d$  indicates that uranium will be transported on average only about 0.5% of the distance that indicator parameters are transported during an excursion. Consequently, uranium concentrations will not increase at the monitoring wells as a consequence of excursion events.

Vandenhove et al. (2009) identified a minimum  $K_d$  in their uranium  $K_d$  data set of 0.9 ml/g at pH  $\geq$  7. This  $K_d$  represents a lower limit for uranium transport at CBR because of the presence of iron oxides and hydroxides and reducing materials in the CBR aquifer solids. Using this minimum  $K_d$  value, the minimum  $R_d$  calculated for the CBR site using equation (3) is 6.6, indicating uranium would be transported, on average, only 15% of the distance that indicator parameters are transported during an excursion. Even using this much smaller, lower-limit  $R_d$  value, uranium transport to the monitoring wells will not occur during an excursion. Because the mined formation at CBR contains minerals such as pyrite, organic carbon, clays and iron oxides and hydroxides that are likely to reduce and sorb uranium even in the presence of high carbonate concentrations, the best-estimate  $K_d$  of 35 and  $R_d$  of 218 are more appropriate for predicting uranium transport at the site.

## References

- EPA (U.S. Environmental Protection Agency). 1999. *Understanding Variation in Partition Coefficient,  $K_d$  Values*. EPA 402-R-99-004B, Office of Air and Radiation, August 1999.
- Freeze, R.A. and J.A. Cherry. 1979. *Groundwater*. Prentice-Hall, Englewood Cliffs, New Jersey.
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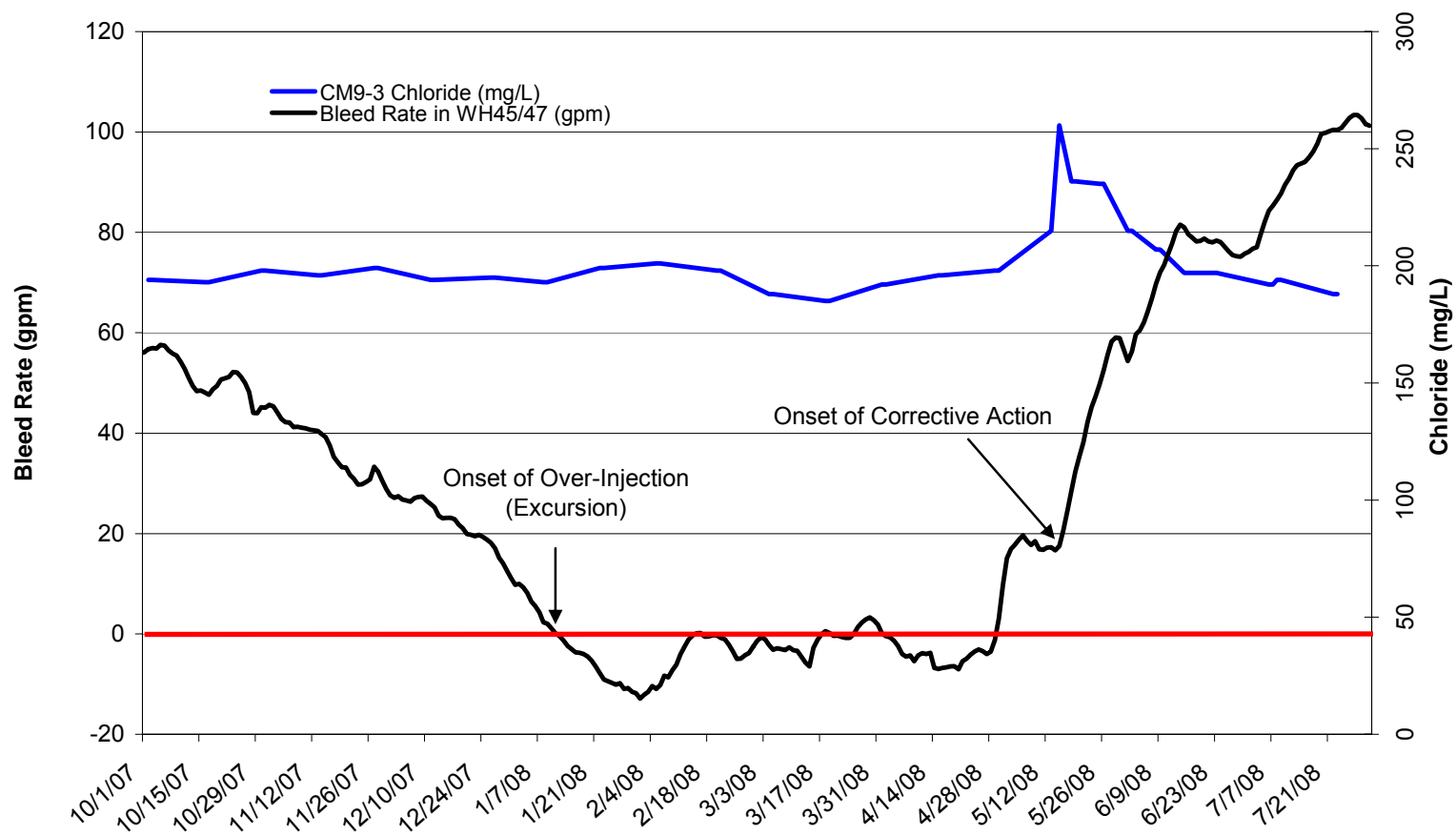
Stewart, C.L. 2002. *The Mineralogy of Uranium Rollfront Deposits and its Significance to In Situ Carbonate Leach Mining*. Masters Thesis, University of Wyoming Department of Geology and Geophysics, August 2002.

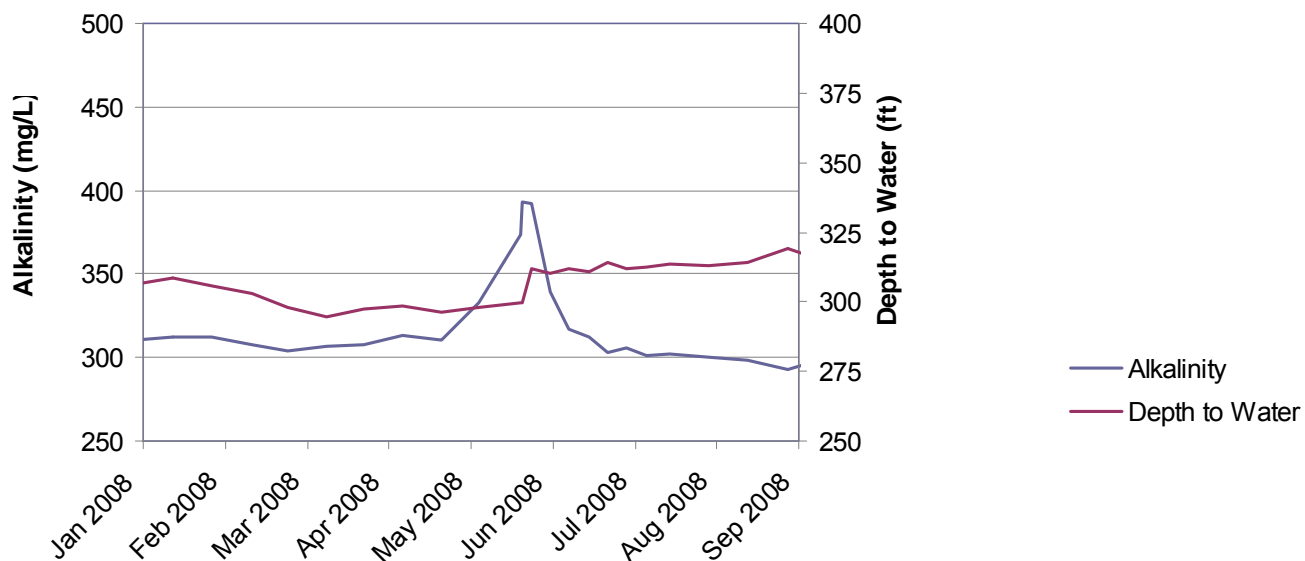
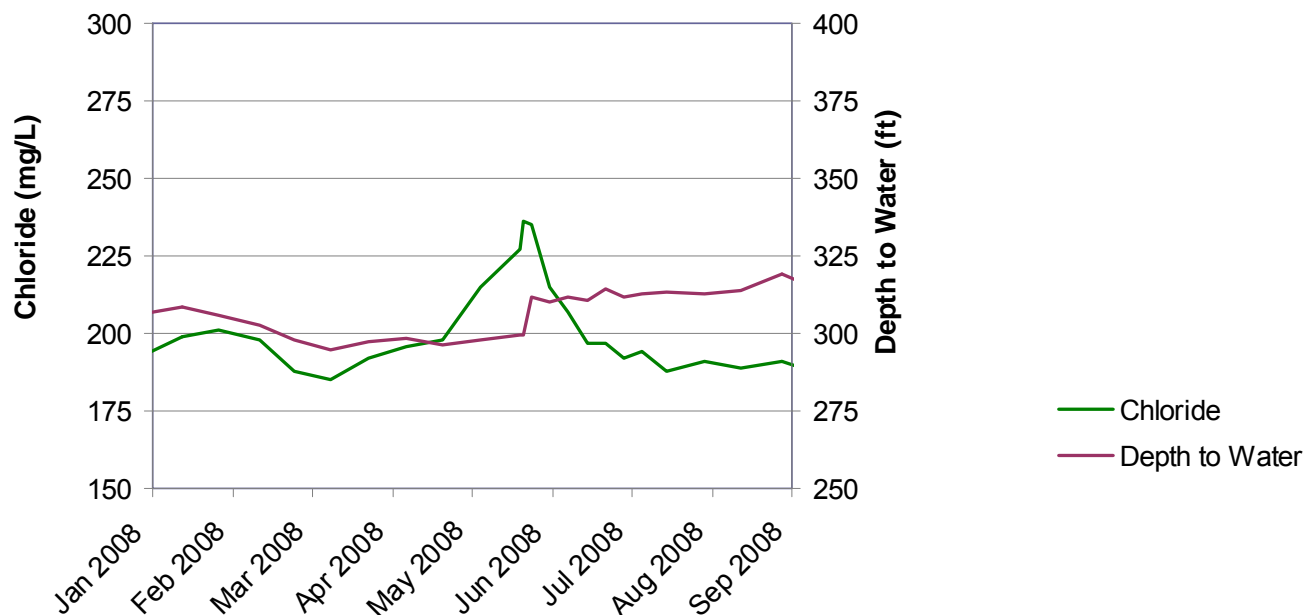
Vandenhove, H., M. Van hess, K. Wouters and J. Wannijn. 2007. Can we predict uranium bioavailability based on soil parameters? Part 1: Effect of soil parameters on soil solution uranium concentration. *Environmental Pollution* 145:587-595.

Vandenhove, H. C. Gil-García, A. Rigol and M. Vidal. 2009. New best estimates for radionuclide solid-liquid distribution coefficients in soils, Part 2. Naturally occurring radionuclides. *Journal of Environmental Radioactivity* 100:697-703.



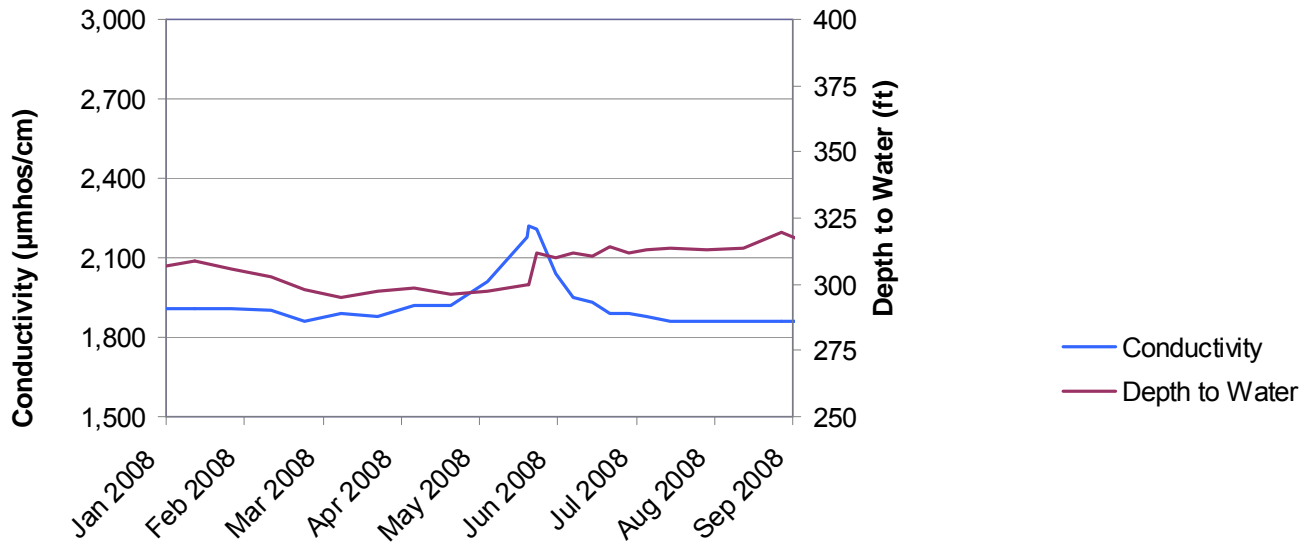
**Figure 1. Water Balance in WH45/47 and Chloride Concentration in CM9-3  
October 2007 Through June 2008**



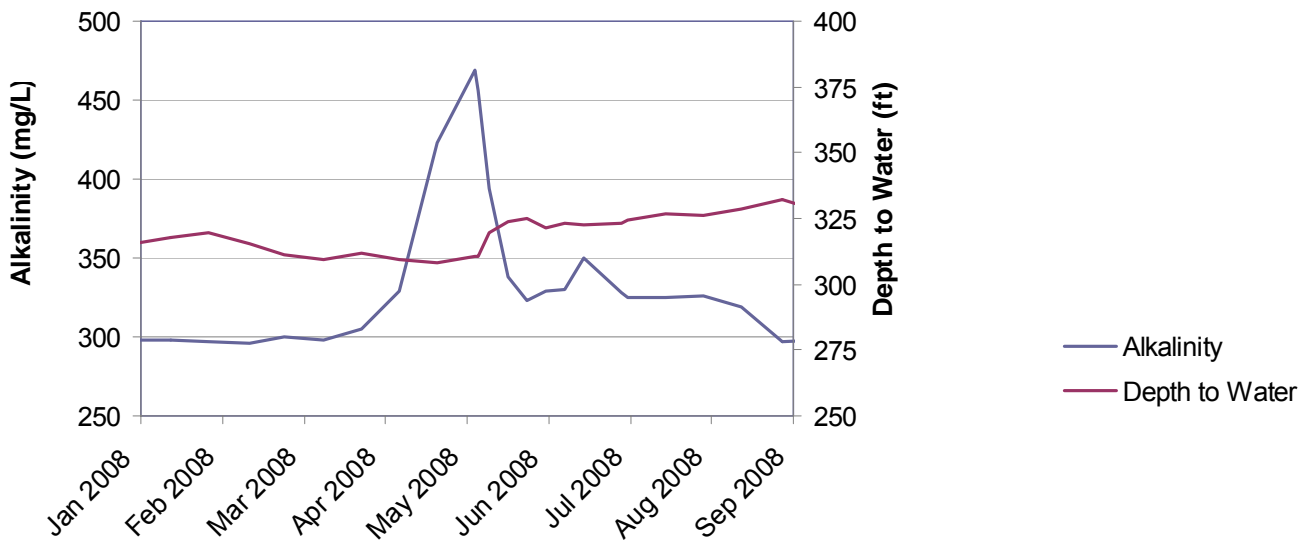
**Figure 2. Well CM9-3 Alkalinity and Water Level Data****Figure 3. Well CM9-3 Chloride and Water Level Data**



**Figure 4. Well CM9-3 Conductivity and Water Level Data**

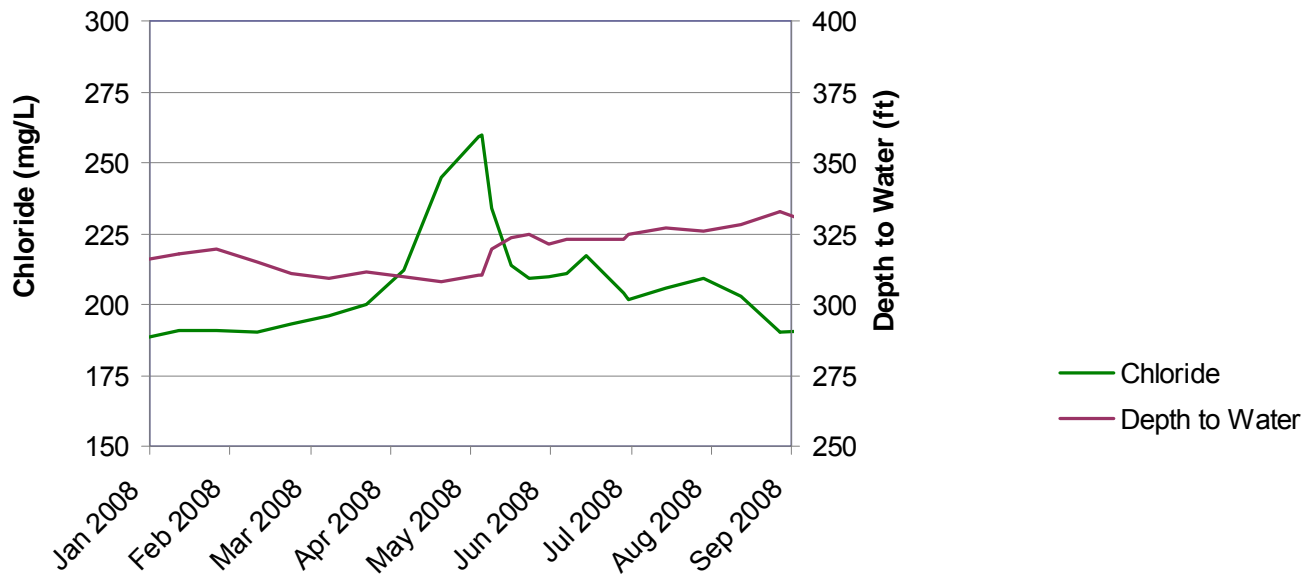


**Figure 5. Well CM9-5 Alkalinity and Water Level Data**

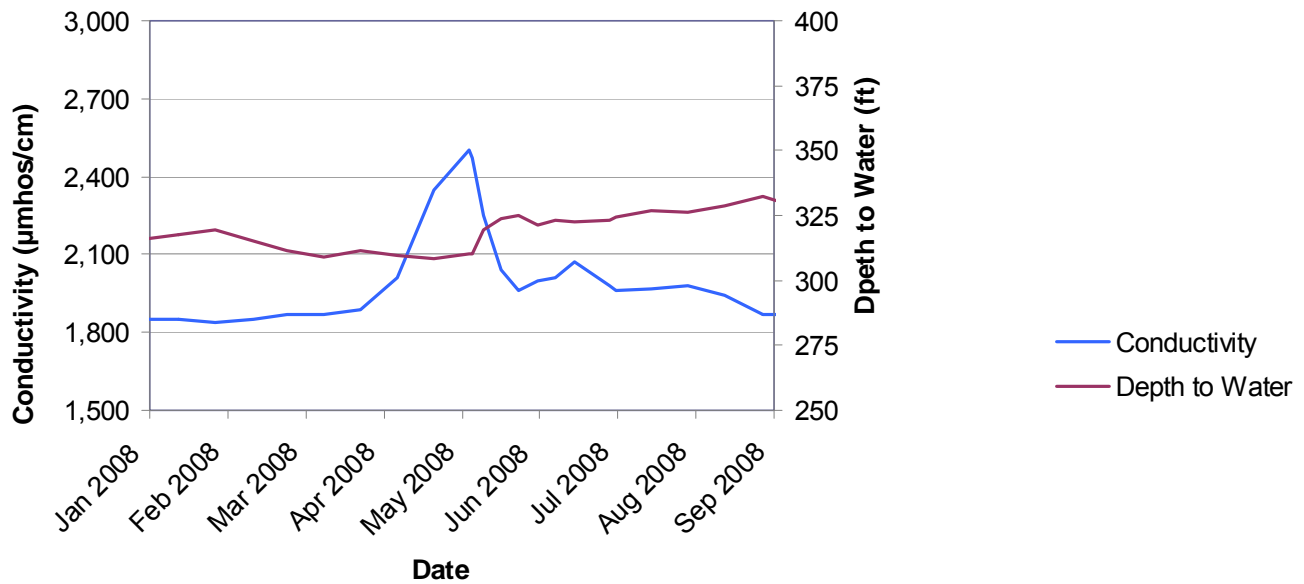




**Figure 6. Well CM9-5 Chloride and Water Level Data**

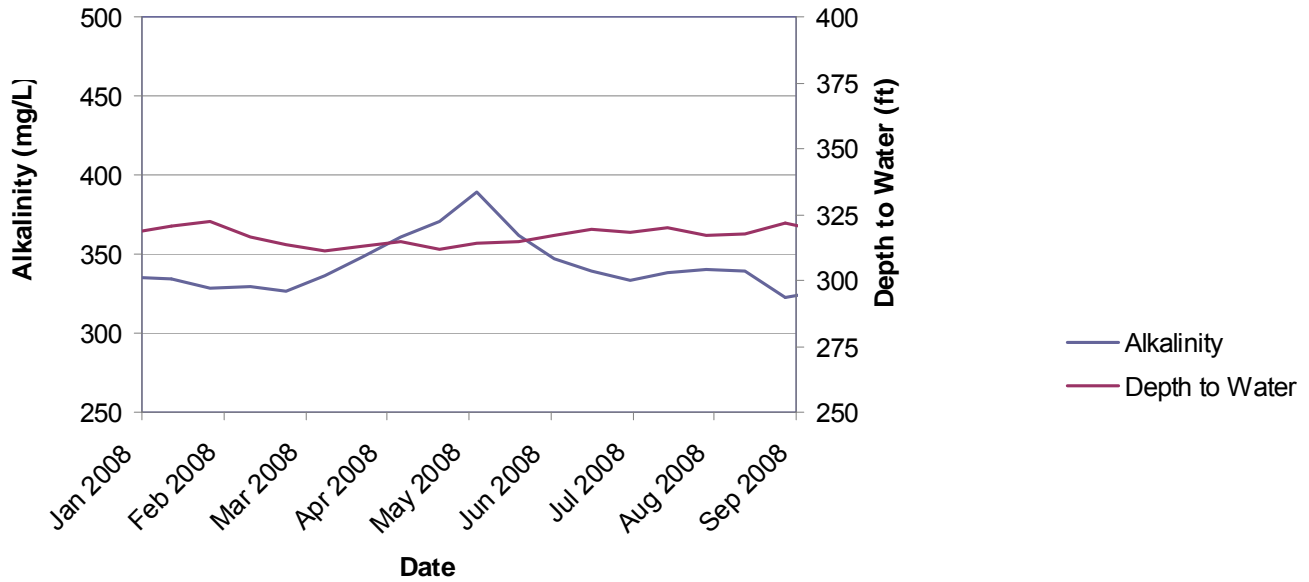


**Figure 7. Well CM9-5 Conductivity and Water Level Data**

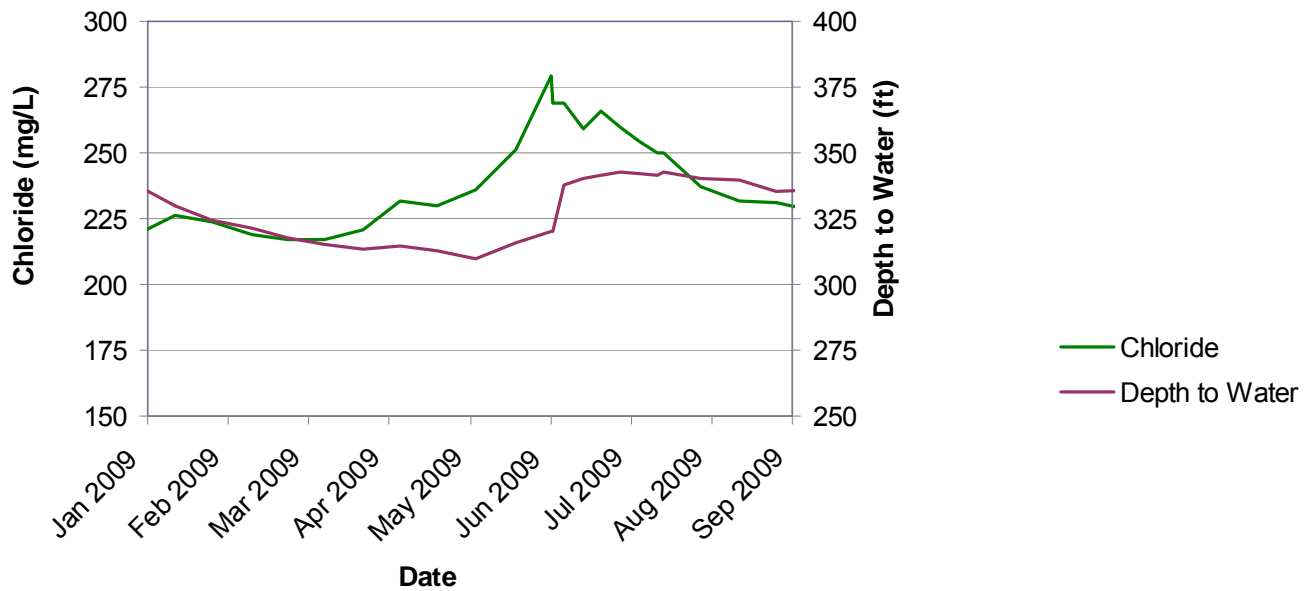




**Figure 8. Well CM9-4 Alkalinity and Water Level Data**

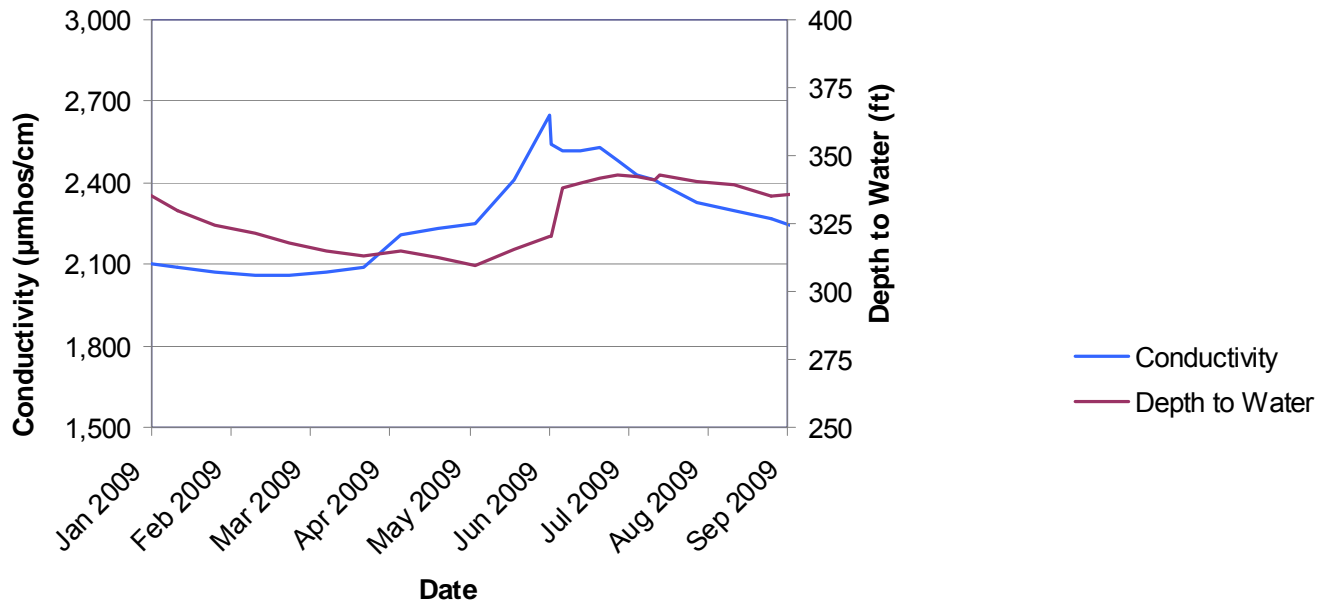


**Figure 9. Well CM9-4 Chloride and Water Level Data**

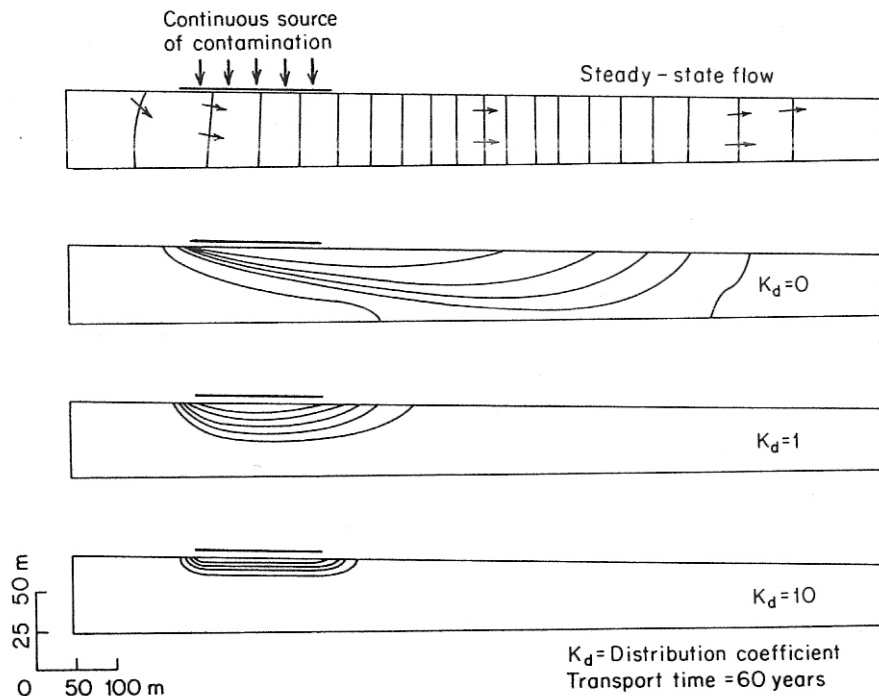




**Figure 10. Well CM9-4 Conductivity and Water Level Data**



**Figure 11. Effects of  $K_d$  Values on Constituent Transport**



Source: Freeze and Cherry (1979)





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CBR-020

Thank you for the opportunity to assist Cameco. If you have questions or comments, please contact me at 303-928-4240.

Sincerely,  
WorleyParsons

A handwritten signature in black ink that reads "Robert Lewis".

Robert Lewis, PG  
Principal Hydrogeologist  
Manager, Environment, Denver