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April 7, 2006

Mr. Norman Shopay California Department of Toxic Substances Control Permitting and Corrective Action Branch 700 Heinz Avenue, Suite 200 Berkeley, California 94710-2721

Subject: Revised Chromium Isotope Study Workplan PG&E Topock Compressor Station, Needles, California

Dear Mr. Shopay:

This letter transmits a revised *Chromium Isotope Study Workplan* for the PG&E Topock Compressor Station. The work plan is submitted in conformance with condition #1 in the California Department of Toxic Substances Control letter dated March 22, 2006.

If you have any questions, please do not hesitate to call me.

Sincerely,

Edine for yvonne Meeks

Enclosure

cc: Kate Burger/DTSC

# **Chromium Isotope Study Workplan**

DATE: April 7, 2006

# 1.0 Introduction

Pacific Gas and Electric Company (PG&E) is addressing chromium in groundwater at the Topock Compressor Station in Needles, California under the oversight of the California Environmental Protection Agency, Department of Toxic Substances Control (DTSC). The Topock Compressor Station is located in eastern San Bernardino County, approximately 15 miles to the southeast of Needles, California (Figure 1).

DTSC has directed PG&E to perform a groundwater study of stable chromium isotope signatures in and around the Topock Facility (DTSC 2006). The objectives of this Chromium Isotope Study are:

- To assess whether chromium isotopes can be used to distinguish anthropogenic chromium (i.e. the chromium releases associated with the Topock Compressor Station) from naturally-occurring chromium in groundwater
- If chromium isotopes can be used to distinguish anthropogenic and naturally-occurring chromium, use the chromium isotopes to assist with delineation of the chromium plume
- Evaluate the utility of chromium isotopes for assessment of the degree of chromium reduction that is occurring in the floodplain area

CH2M HILL is coordinating with the U.S. Geological Survey (USGS) to plan and conduct the Chromium Isotope Study.

# 2.0 Background

# 2.1 Chromium Chemistry

Chromium (Cr) is the 17<sup>th</sup> most common element in rocks that compose the earth's crust (Hem 1970), and it can enter the environment naturally through weathering of chromiumcontaining minerals and leaching from soils as well as from discharges from industrial sources (Kimbrough and others, 1999). In aqueous solutions chromium exists as trivalent chromium (Cr[III]) and hexavalent chromium (Cr[VI]). Cr(III) is the predominant form under moderately oxidizing to reducing conditions over a wide range of pH (Ball and Nordstrom, 1998), though it readily forms insoluble precipitates and adsorbs strongly onto minerals in the aquifer matrix. As a result, Cr(III) concentrations are typically very low (i.e., less than 10 micrograms per liter  $[\mu g/L]$ ) in near-neutral pH waters. Cr(VI) is the predominant form only under strongly oxidizing conditions (Rai and Zachara 1984). Sorption/desorption reactions on aluminum and iron oxide mineral surfaces govern chromium solubility. The different oxidation states have very different adsorption characteristics because of their oppositely charged valences. Cr(VI) forms negatively charged ions when dissolved in water, in contrast to Cr(III) which forms positively charged ions. Cr(III) is therefore much more strongly adsorbed than Cr(VI). Cr(III) sorption increases with increasing pH and is associated with iron-rich surface coatings (Rai and Zachara 1984). Cr(VI) sorption decreases at high pH, and in some studies sorption has been shown to decrease with increasing ionic strength (Rai and Zachara 1984). Reduction of Cr(VI) to Cr(III) can occur under a variety of conditions -- even in oxic environments; and reduction of Cr(VI) to Cr(III) in anaerobic environments in the presence of sulfide or ferrous ions is almost instantaneous.

### 2.2 Chromium Isotope Theory

There are four stable isotopes of Cr having atomic masses of 50, 52, 53, and 54 ( $^{50}$ Cr,  $^{52}$ Cr,  $^{53}$ Cr and  $^{54}$ Cr), with 52 by far the most common. There are no stable isotopes of any other element having atomic masses of 52 or 53. Small variations in the ratio of  $^{53}$ Cr to  $^{52}$ Cr are expected to occur in nature and may have the potential to identify specific chromium sources or chemical processes involving Cr (Ball and Bassett 1999; Ball et al. 2001). Reduction of oxidized aqueous species of other redox sensitive elements such as sulfur (SO<sub>4</sub><sup>2-</sup>) (Harrison and Thode 1957; Brüchert et al. 2001) and selenium (SeO<sub>4</sub><sup>2-</sup>) (Johnson et al. 1999) tends to enrich the products in the light isotopes because they preferentially react, and the residual reactants become progressively enriched in the heavier isotopes as reduction proceeds. In these cases, the breakage of the bond with oxygen requires significant energy promoting the isotopic fractionation, and is the rate-limiting step in the reduction reaction. If Cr behaves the same way, then variations in the isotopic composition of Cr in groundwater along a flowpath from a suspected Cr source could be used to determine the extent of Cr reduction that has occurred.

Ellis et al. (2002) demonstrated that Cr isotopes are substantially fractionated during abiotic reduction of Cr(VI) to Cr(III). For example, progressive reduction of Cr(VI) in a magnetite slurry, buffered at pH~6 in order to minimize sorption of Cr<sub>2</sub>O<sub>4</sub><sup>2-</sup> and HCr<sub>2</sub>O<sub>4</sub><sup>-</sup>, resulted in progressively increasing  $\delta^{53}$ Cr of the remaining dissolved Cr(VI) ( $\delta^{53}$ Cr is the per mil difference in measured  ${}^{53}$ Cr/ ${}^{52}$ Cr relative to that of N.I.S.T. 979, an accepted Cr isotope standard). Using a Rayleigh fractionation model, in which Cr(III) once produced is immediately removed from further reaction (e.g., by sorption onto mineral surfaces), an instantaneous fractionation factor ( $\propto_{Cr(III)-Cr(VI)} = 0.9965$ ) was calculated for the reduction reaction. Using this factor, after the reaction progressed to 80 percent completion the remaining Cr(VI) had  $\delta^{53}$ Cr 5.6 per mil greater than the original Cr(VI); at 90 percent completion, the difference was greater than 8 per mil; and so on. Cr reduction experiments utilizing natural magnetite-bearing and microbe-rich aquifer sediments, including autoclaved controls, gave essentially identical results, suggesting that at least for these sediments the reduction mechanism was abiotic.

Ellis et al. (2004) demonstrated that Cr isotopes are not significantly fractionated during sorption of Cr(VI) aqueous species onto Al<sub>2</sub>O<sub>3</sub> and goethite substrates at circum-neutral pH. Similarly, no significant fractionation was observed during sorption of Cr(VI) onto Al<sub>2</sub>O<sub>3</sub> at pH=4. In contrast, a kinetic isotope effect was observed during sorption of Cr(VI) onto goethite at pH=4, with  $\delta^{53}$ Cr of the initial sorbed Cr(VI) being 3.5 per mil less than that of the coexisting aqueous Cr(VI); however, the isotopic contrast essentially disappeared as the 12-hour experiment progressed. Thus, these investigators concluded that sorption of Cr(VI) probably has only a secondary effect on the isotopic composition of dissolved Cr along

groundwater flowpaths in most natural aquifer systems, although effects may be magnified at plume edges or fronts.

Equilibrium isotope fractionation between aqueous Cr(III) and Cr(VI) may be important in situations where the Cr(III)/Cr(VI) ratio of dissolved species is large (i.e., >1). Theoretical estimates of equilibrium Cr isotope fractionation between Cr aqueous species at 25°C (Schauble 2004) indicate that  $\delta^{53}$ Cr of Cr(VI) will be ~6.6 per mil greater than that of Cr(III). Experiments are currently underway at the USGS in Menlo Park, CA to determine the practical fractionation factors of the equilibrium process, as well as to determine if natural Cr oxidation mechanisms such as oxidation of Cr(III) on mixed-valence manganese oxide surfaces promote fractionation of the Cr isotopes. However, it is important to recognize that the equilibrium effect on  $\delta^{53}$ Cr of Cr(VI) will decrease as the Cr(III)/Cr(VI) ratio of dissolved species decreases (i.e., at higher pH), due to isotope mass balance considerations.

# 2.3 Existing Data on Chromium Isotopes in the Mojave Basin

The USGS is beginning to establish a database of Cr isotope compositions in groundwater from both anthropogenic and natural settings. The database includes isotopic data from aquifers contaminated by Cr plating wastes associated with industry and military activities and uncontaminated aquifers in the Mojave Desert of Southern California where groundwater naturally contains elevated levels of dissolved Cr(VI). Based on existing USGS data, for groundwater samples collected nearest to sources of unambiguous anthropogenic Cr contamination,  $\delta^{53}$ Cr of dissolved Cr(VI) is approximately 0.0 per mil, similar to Cr in igneous minerals (Ellis et al. 2002; Johnson and Bullen 2004) and thus to potential mineral sources of the Cr. At the sites the USGS has studied to date, Cr(VI)-bearing groundwater downgradient from the contamination sources consistently has  $\delta^{53}$ Cr > 0.0 per mil, with values generally increasing as Cr(VI) concentrations decrease, indicating that Cr(VI) reduction is probably occurring as the contaminant plume migrates through the aquifer materials. A sample collected in 2001 from a monitoring well in the PG&E Hinkley Facility groundwater plume had a  $\delta^{53}$ Cr value of 0.09 per mil (John Izbicki, personal communication, March 2006). The well was located approximately 800 feet downgradient of the suspected source of Cr(VI) at that facility.

Groundwater samples collected by the USGS from the Mojave Desert containing naturally elevated levels of Cr(VI) (Ball and Izbicki 2004) likewise have  $\delta^{53}$ Cr ranging from around 0 to over 4 per mil (Ball et al. 2001 and other unpublished analyses determined at USGS, Menlo Park). This indicates that either Cr(VI) reduction or equilibrium between Cr(III) and Cr(VI) aqueous species has occurred along flowpaths between the recharge zone and the sample locations in this arid region. The USGS has rarely analyzed a groundwater sample that has  $\delta^{53}$ Cr < 0.0 per mil, which has been interpreted to indicate a considerable store of isotopically light Cr exists, bound to aquifer mineral surfaces.

# 2.4 Application of Cr Isotope Analyses to Evaluate Potential Sources

The spatial distribution of Cr isotope compositions in groundwater throughout a Cr plume may be evaluated based on potential fractionation patterns. It appears that reduction of dissolved Cr(VI) is an important mechanism that causes measurable Cr isotope fractionation in aquifers. Therefore, if the concentration and Cr isotope composition of the suspected source of Cr along a flowpath is known, then the Cr isotope composition of downgradient

samples possibly can be predicted based solely on their measured Cr(VI) concentrations using a simple Rayleigh model and the fractionation factor reported by Ellis et al. (2002). For example, if  $\delta^{53}$ Cr of the suspected source of Cr(VI) is 0 per mil and the concentration is 1 part per million (ppm), then a downgradient groundwater sample having 0.1 ppm Cr(VI) (i.e., 90 percent completion of the reduction reaction) would be expected to have  $\delta^{53}$ Cr of about 8 per mil if reduction of Cr(VI) was the only process causing decreasing Cr concentrations along the flowpath. If the Cr isotope composition of the downgradient water sample is not as great as that predicted by the fractionation model, then the Cr in that downgradient water sample possibly was not derived from the suspected Cr source or the sample has been diluted by Cr having a different isotopic composition from another source. Because both uncontaminated groundwater and contaminated groundwater that has been reduced can have  $\delta^{53}$ Cr greater than 4.5 per mil, Cr isotopes cannot be used alone to determine the source of Cr in an aquifer system. The use of Cr isotopes assumes that hydrologic factors that can cause decreasing concentrations of dissolved constituents (e.g., dispersion, diffusion, mixing) can be taken into account using additional geochemical parameters. A possible approach to compensate for these effects would be to index the Cr(VI) concentration to that of a conservative constituent of the plume water that is absent or is known to be different in the uncontaminated regional groundwater.

# 2.5 Study Limitations

As the above discussions indicate, studies of <sup>53</sup>Cr in the environment have only recently been conducted. This is a relatively new science, in which stable isotopes of environmentally sensitive elements have been applied to test sites. Investigators in environmental isotope studies for selenium, which has undergone more isotopic study than chromium, caution that effects of all important processes on isotopic fractionation must be understood before more quantitative use of stable isotopic ratios may be realized (Johnson and Bullen 2004). For example, adsorption of Cr(VI) may cause significant isotopic fractionation in areas of low Cr(VI) concentrations, such as background areas or plume edges (Ellis et al. 2002).

Other processes may also cause chromium isotope fractionation, such as plant uptake and precipitation reactions, but effects of these processes have not yet been documented in the literature. Selenium, a geochemically similar element, has shown fractionation by algal assimilation (Johnson 2004), so other forms of plant uptake may produce similar effects for chromium.

These observations provide perspective that although the use of chromium isotopes may provide a useful tool for the present study, the science is in a relatively early stage and its use may have significant limitations at the Topock site.

# 3.0 Study Approach

# 3.1 Samples to be Collected

To determine the isotopic composition of Cr in groundwater underlying the PG&E Topock Compressor Station and surrounding area, groundwater samples will be collected from 27 monitoring and water-supply wells. The samples will be collected from seven wells within the plume in the alluvial fan deposits, three wells in the plume in the floodplain deposits, eight wells considered to be immediately outside the plume margins, and nine wells considered to be background wells on the California side of the river. Table 1 at the end of this memorandum provides a listing of the wells to be sampled. Figure 2 shows the locations of wells to be sampled for this study.

The sample from the CA Agricultural Station will be used as a test sample to determine quantification limits for the isotopic analysis. This well has historically shown Cr(VI) concentrations around  $1 \mu g/L$ . The analytical method for chromium isotopes requires a minimum mass of chromium to be loaded to the mass spectrometer, so that small concentrations require a larger volume of groundwater sample. Salinity of groundwater may cause interferences in the cation exchange sampling technique and excessive salts may mask the mass spectrometer signal in the laboratory. The quantitation limit is therefore dependent on the combination of Cr(VI) concentration and salinity. If a second phase of sampling is warranted, this analysis will be used to determine whether low-Cr(VI) wells may be sampled.

The sample from well MW-39-60 will be collected but not analyzed unless it contains Cr(VI) at a quantifiable concentration for isotope analysis. If warranted, analysis of this sample will take place during the second phase.

The group of wells in Table 1 is believed to represent the local geologic environment of the southwestern corner of Mohave Valley. The source rocks for the alluvial deposits at all alluvial wells are the metamorphic and sedimentary rocks of the Chemehuevi and Sacramento Mountains that lie between Needles and Topock Canyon. Fluvial wells included in the study are limited to those on the Topock Site where Cr(VI) is present in measurable concentrations. Shallow fluvial wells typically exhibit reducing conditions and do not contain detectable concentrations of Cr(VI). Longer screened supply wells such as the Lily Hill Well and the CA Agriculture Station Well are expected to display the same fractionation pattern as the shorter screen monitoring wells at the Topock Site, as the geologic environment is similar and reducing conditions are not evident in most alluvial wells. Reducing conditions have only been observed in a few very deep alluvial wells onsite, and the two wells referenced above do not penetrate to the base of the alluvian.

Following initial analysis, if additional data are required to determine whether a distinction between plume and reference wells can be discerned, or to assist with further delineation of the chromium plume, a second phase of sampling will be conducted in which additional selected wells will be sampled and analyzed. The list of potential wells for this second phase is shown in Table 2, and include Arizona wells along with additional plume and plume margin wells. Further discussion of this decision process on the need for a second phase of sampling is provided in Section 3.4.

# 3.2 Sample Collection and Analysis

USGS personnel will accompany the CH2M HILL field team during its regular sampling rounds. The CH2M HILL field team will purge the wells and sample for general chemistry parameters. The USGS will be responsible for collection, transport, and analysis of all Cr isotope samples collected for this study.

Standard well purging procedures to be used in association with the study are presented in the Field Procedures Manual (CH2M HILL 2005). The Field Procedures Manual presents standardized protocols for field investigation and data collection activities for the several

investigation, monitoring, and interim measure programs performed at the Topock Compressor Station.

The USGS sample will be filtered using a 0.2-micrometer filter. A small aliquot of each sample will be taken for measurement of total Cr. The remainder of each sample will then be processed in the field using the cation exchange method for field speciation of Cr(VI) (Ball and McCleskey 2003). Cr(III) will be sorbed on cation exchange resins leaving only Cr(VI) in the liquid fraction. All liquid samples will be preserved to pH <2 using ultra-clean hydrochloric acid. Both the unspeciated and speciated liquid samples will be sent to the USGS laboratory in Boulder, CO for analysis of total Cr by graphite furnace atomic absorption spectroscopy. The sample processed using the cation-exchange method contains only Cr(VI). The second sample will contain Cr(total); therefore, Cr(III) will be determined by difference.

The chromium isotope composition of the Cr(VI) liquid sample will be determined in the USGS laboratory in Menlo Park, CA. The Cr(III) fraction retained on the cation exchange resin may be determined if sufficient Cr is scavenged by the resin column. Analysis will be accomplished using thermal-ionization mass spectrometry (TIMS) by application of purified Cr to a solid source filament using the silica gel technique to enhance production of thermal ions (Ball 1996). This technique has been applied successfully in the groundwaters from the Mojave Desert. Analyses of samples of water from 16 wells in the Twenty-Nine Palms area of the Mojave Desert show  $\delta^{53}$ Cr values range from 0.1 to 4.5 per mil, with an average precision of  $\pm$  0. 1 per mil. Duplicate samples will be collected from a minimum of 10 percent of the wells (i.e., at least three wells). Duplicates will be chosen at wells from the low, middle, and upper areas of the Cr(VI) concentration distribution.

Samples collected by the CH2M HILL team (either as part of the BGS, GMP, or the present study) will be analyzed by the suite of general chemistry parameters shown in Table 3. Holding times and quality assurance/quality control procedures will follow standard procedures (CH2M HILL 2005).

The water quality and isotopic data will be coupled with detailed geologic data available at the site to evaluate changes in chromium concentration, speciation, and isotopic composition in the zone of contamination, both areally and with depth as groundwater moves away from the contamination source. It is expected that the stable isotopes of oxygen and hydrogen can be used to help identify the mixing of groundwater of different sources.

# 3.3 Quality Control and Data Management

Quality control procedures will be implemented for both field activities and laboratory work associated with the study. Detailed descriptions of quality control procedures specific to water quality sampling at the Topock site are provided in the *Quality Assurance Project Plan for Water Quality Sampling and Analysis* (QAPP) (Appendix D of the Topock Field Procedures Manual [CH2M HILL 2005]). The quality control procedure used during laboratory purification of Cr fractions and measurement of Cr isotopic compositions involves processing of the NIST 979 Cr reference metal through the entire analytical procedure several times over the course of the study, and demonstrating consistency and accuracy of derived Cr isotopic compositions. Quality Control procedures followed by USGS personnel are described in McCleskey et al. (2004).

## 3.3.1 Data Validation

The analytical results of groundwater and surface water samples will be evaluated to verify whether the data are sufficiently accurate, precise, and representative of site conditions for decision-making purposes in support of ongoing site investigation and remediation activities. Details regarding data validation are provided in the QAPP (CH2M HILL 2005).

## 3.3.2 Data Management

Management of data generated from the study will be conducted in accordance with the *PG&E Program Data Management Plan* (CH2M HILL 2004). The Data Management Plan outlines standardized procedures for field data collection and review, analytical data loading into the information system (environmental database), verification of the uploaded data, quality assurance/quality control procedures associated with data management, and reporting formats.

## 3.4 Data Evaluation

The objective of this sampling, as stated in Section 1, is to determine whether chromium isotopes may be used as a tool to distinguish Topock plume groundwater from natural Cr(VI) in the area. Data evaluation will be a cooperative effort between CH2M HILL and the USGS. Both parties will conduct statistical and geochemical analysis of data, and will compare results during regular communications. It is anticipated that CH2M HILL will utilize the groundwater flow model and possibly geochemical modeling to test flowpath and mixing scenarios. The USGS will assist in writing the report and will provide review of the report to be submitted to DTSC.

Initially, reference wells and plume wells will be compared to assess whether there is a statistically significant difference between the two groups. Analysis tools in this step would be a t-test if samples are shown to be normally distributed using a chi-squared statistical test. If the data are not normally distributed, a non-parametric set of statistical tests will be utilized, dependent upon the distribution of values. Outliers in either group will be considered for deletion, reanalysis, or reassignment to another group on the basis of geochemical and geologic properties of the sample sources. For example, geochemical data may indicate that a sample shows no characteristics of a plume sample, and the isotope data support this, so that sample may be reassigned to the reference well group. The USGS and CH2M HILL will meet approximately three weeks into the data analysis process to gain consensus on whether the data show a clear distinction.

A second phase of data collection will be recommended in either of the following cases:

- 1. Data indicate a potential separation between the two groups and additional data are needed to clarify this distinction. In this case, additional plume and reference wells would be sampled to increase the sample populations for each group.
- 2. Data indicate a clear distinction between plume and reference groups. In this case additional wells would be sampled in Arizona and near the plume margins to help better define the plume extent.

Stable chromium isotope ratios will be assessed to both distinguish natural and anthropogenic sources and to evaluate whether Cr(VI) has been reduced significantly in both plume and non-plume environments.

Concentrations of Cr(VI) that could be naturally occurring in this area range up to about 40  $\mu$ g/L, based on observed data collected in the Background Study thus far and from published reports on the nearby Mojave Desert area (Ball and Izbicki 2004). Chromium isotopes may be effective in distinguishing samples in this concentration range between plume edge and non-plume naturally occurring samples. Plume edge samples are expected to show a chromium isotopic signature that is slightly above 0.0 per mil for  $\delta^{53}$ Cr, whereas the same concentration in non-plume groundwater may show a significantly more elevated value as a result of partial reduction down a long flowpath (i.e. several miles) from its original source. However, if a sample is drawn from a partially-reduced area of the plume, such as in the floodplain, then plume water may also show a significantly elevated  $\delta^{53}$ Cr value. As discussed above, adsorption reactions near the plume edge may also cause fractionation that would artificially raise the  $\delta^{53}$ Cr value (Ellis et al. 2004). Reducing conditions that would cause fractionation will be assessed using geochemical data (ORP, nitrate/ammonia, manganese, iron, organic carbon) as well as geologic evidence (e.g. gray color in core indicating reduced sediments).

General chemistry parameters such as nitrate, ammonia, iron, manganese, and dissolved organic carbon will be used in conjunction with the isotope data to illustrate that Cr(VI) reduction is occurring along a flowpath. The major ions sodium, calcium, magnesium, chloride, bicarbonate, and sulfate will be used to "fingerprint" waters to either distinguish groups of waters or to chart changes along a flowpath. Mixing of plume water with non-plume water that could be suggested by isotopes may be tested independently using geochemical modeling of major and minor parameters. Field parameters of pH, ORP, specific conductance (SC), and temperature will also be used to show reductive environments, evaluate water groups, and estimate mixing.

Stable isotopes of oxygen and hydrogen have been collected as part of the Topock Groundwater Monitoring Program (GMP) and the Groundwater Background Study (GBS) over the past one to two years. Though many of the data overlap in plume margin areas, three isotope signatures can be interpreted in three groups: industrial water (from the compressor station), non-industrial groundwater (natural signature range), and river water. The use of these data in tandem with chromium stable isotope data may clarify the distinction between groups. A discussion of recent oxygen and hydrogen isotope data was provided in the Annual Performance Monitoring Evaluation for the Topock Interim Measure (CH2M HILL 2006). Figure 3 shows the distribution of these isotopes and the inferred groupings.

# 3.5 Project Schedule

The schedule for the implementation of the Chromium Isotope Study is provided in Table 4. The implementation schedule is subject to obtaining work plan approval from DTSC, as well as access to offsite wells.

# 4.0 Certification

This work plan was prepared by CH2M HILL under the supervision of the professional whose seal and signature appears hereon, in accordance with currently accepted professional practices; no warranty, expressed or implied, is made.

Trian Shroth

Brian Schroth, Professional Geologist #7423

# 5.0 References

- Arar, E.J., Long, S.E., and Pfaff, J.D. 1991. Determination of dissolved hexavalent chromium in drinking water, groundwater and industrial wastewater effluents by ion chromatography. U.S. Environmental Protection Agency, Method 218.6, revision 3.0.
- Ball, J.W. 1996. *Thermodynamic and isotope systematics of chromium chemistry*. Ph.D. Dissertation, University of Arizona, 288 p.
- Ball, J.W., and Izbicki. 2004. Occurrence of hexavalent chromium in ground water in the western Mojave Desert, California. Applied Geochemistry, Vol. 19, p. 1123-1135
- Ball, J.W. and McCleskey. 2003. A new cation-exchange method for accurate field speciation of hexavalent chromium. *Talanta*, Vol. 61, p. 305-313.
- Ball, J.W., and Nordstrom, D.K. 1998. "Critical evaluation and selection of standard state thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides, and hydroxides." *Journal of Chemical and Engineering Data*, Vol. 43, p. 895-918.
- Ball, J.W., and Bassett, R.L. 1999. "Ion exchange separation of chromium from natural water matrix for stable isotope mass spectrometric analysis." *Chemical Geology*, Vol. 168, pp. 123-134.
- Ball, J.W., Bullen, T.D., Izbicki, J.A., and Johnson, T.M. 2001. "Stable isotope variations of hexavalent chromium in groundwaters of the Mojave Desert, California, USA." *Geological Society of America Abstracts with Programs*, Vol. 33, p. A-111.
- Brüchert, V., Knoblauch, C., Jorgensen, B.B. 2001. Controls on stable sulfur isotope fractionation during bacterial sulfate reduction in Arctic sediments. *Geochimica et Cosmochimica Acta*, Vol. 65, p. 763-776.
- California Department of Toxic Substances Control (DTSC). 2006. Requirement for chromium isotope study, Pacific Gas & Electric Company, Topock compressor station, Needles, California. EPA ID No. CAT080011729. Letter to Yvonne Meeks (PG&E), January 13.

CH2M HILL. 2004. PG&E Program Data Management Plan. Report to PG&E. November.

- CH2M HILL. 2005. Sampling, Analysis, and Field Procedures Manual, PG&E Topock Program, Revision 1. Report to PG&E. March 31.
- CH2M HILL. 2006. Performance Monitoring Report for Fourth Quarter 2005 and Annual Performance Evaluation, February 2005 through January 2006, Interim Measures Performance Monitoring Program. Report to PG&E. March 15.
- Ellis, A.S., T.M. Johnson, and T.D. Bullen. 2002. "Chromium isotopes and the fate of hexavalent chromium in the environment." *Science*, 295, 2060-2062.
- Ellis, A.S., Johnson, T.M., and Bullen, T.D. 2004. Using chromium stable isotope ratios to quantify Cr(VI) reduction: lack of sorption effects. *Environmental Science & Technology*, Vol. 38, p. 3604-3607.
- Harrison and Thode. 1957. The kinetic isotope effect in the chemical reduction of sulphate. *Transactions of the Faraday Society*, Vol. 53, p. 1648-1651
- Hem, J.D. 1970. *Study and interpretation of the chemical characteristics of natural water, second edition*. U.S. Geological Survey Water Supply Paper 1473, 363 p.
- Johnson, T.M. 2004. A review of mass-dependent fractionation of selenium isotopes and implications for other heavy stable isotopes. *Chemical Geology*, Vol. 204, p.201-214.
- Johnson, T.M. and T.D. Bullen. 2004. "Mass-dependent fractionation of selenium and chromium isotopes in low-temperature environments." In *Geochemistry of Non-Traditional Isotopes. Reviews in Mineralogy and Geochemistry*, 55, 289-317.
- Johnson, T.M., Herbel, M.J., Bullen, T.D., and Zawislannski, P.T. 1999. Selenium isotope ratios as indicators of selenium sources and oxyanion reduction. *Geochimica et Cosmochimica Acta*, Vol. 63, p. 2775-2783.
- Kimbrough, D.E., Cohen, Y., Winer, A.M., Creelman, L., and Mabuni, C. 1999. "A critical assessment of chromium in the environment." *Critical Reviews in Environmental Science and Technology*. Vol. 29, pp. 1-46.
- McCleskey, R.B., Nordstrom, D.K., and Naus, C.A. 2004. Questa Baseline and Pre-Mining Ground-Water-Quality Investigation. 16. Quality Assurance and Quality Control for Water Analyses. USGS Open-File Report 2004-1341. 105 p.
- Rai, D., and Zachara, J.M. 1984. Chemical attenuation rates, coefficients, and constants in leachate migration, Volume 1: A critical review. EA-3356, Electric Power Research Institute, Palo Alto, California, variously paged.
- Schauble, E.A. 2004. Applying stable isotope fractionation theory to new systems. *Reviews in Mineralogy*. Vol. 55, p. 65-111.

# Tables

#### TABLE 1

Chromium Isotope Study – Proposed Sample Locations, Phase I Chromium Isotope Study Workplan

Location, Sampling Plan	Depth Interval	Comments
California Background		
MW-16 Background Program	Top 19' of water table; 198 to 217' bgs	Avg. 9.7 μg/L Cr(VI)
MW-17 Background Program	Top 19.5' of water table; 130 to 149.5' bgs	Avg. 4.8 μg/L Cr(VI)
MW-18 Background Program	Top 19' of water table; 85 to 104' bgs	Avg. 29.4 μg/L Cr(VI)
CW-01M Compliance Monitoring Program	Intermediate Depth Interval; 140 to 190' bgs	Avg. 15.5 μg/L Cr(VI)
CW-02M Compliance Monitoring Program	Intermediate Depth Interval; 155 to 205' bgs	Avg. 14.2 μg/L Cr(VI)
OW-03S Compliance Monitoring Program	Shallow Depth Interval; 86 to 116' bgs	Avg. 17.1 μg/L Cr(VI)
OW-03M Compliance Monitoring Program	Intermediate Depth Interval; 180 to 200' bgs	Avg. 13.8 μg/L Cr(VI)
Lily Hill Background Program	20 to 220' bgs	Avg. 10.5 $\mu$ g/L Cr(VI), irrigation well for Needles apartment complex
CA Agricultural Station Background Program	Well depth of 202' (screened interval unknown)	Avg. 2.0 μg/L Cr(VI), irrigation well for Agricultural Station
Plume Margin Wells (all are alluv	vial fan wells)	
MW-13 GMP	Top 20' of water table; 28.5 to 48.5' bgs	Avg. 18.0 μg/L Cr(VI)
MW-14 GMP	Top 20' of water table; 111 to 131' bgs	Avg. 33.1 μg/L Cr(VI)
MW-33-90 GMP	Intermediate depth well; 69 to 88' bgs	Avg. 13.6 μg/L Cr(VI)
MW-33-210 GMP	Deep well; 190 to 210' bgs	Avg. 4.2 μg/L Cr(VI)
MW-35-60 GMP	Shallow depth well; 38.5 to 58.5' bgs	Avg. 26.4 μg/L Cr(VI)
MW-35-135 GMP	Deep well; 120 to 140' bgs	Avg. 15.3 μg/L Cr(VI)
MW-37S GMP	Intermediate depth well; 64 to 84' bgs	Avg. 5.2 μg/L Cr(VI)
MW-40S GMP	Shallow depth well; 115 to 135' bgs	Avg. 5.4 μg/L Cr(VI)

Location, Sampling Plan	Depth Interval
Chromium Isotope Study – Proposec Chromium Isotope Study Workplan	3 Sample Locations, Phase I
TABLET	

Location, Sampling Plan	Depth Interval	Comments
Plume: Alluvial Fan Deposits		
MW-10 GMP	74 to 94' bgs	Avg. 1,800 $\mu g/L$ Cr(VI), adjacent to plant, shallow well
MW-38S GMP	75 to 95' bgs	Avg. 740 μg/L Cr(VI), downgradient of MW-10, shallow well
MW-24B GMP	194 to 214' bgs	Avg. 5,200 μg/L Cr(VI), downgradient from MW-38 cluster; shallow well
MW-25 GMP	84 to 104' bgs	Avg. 1,900 $\mu$ g/L Cr(VI), upgradient of MW-20 bench, shallow well
MW-20-70 GMP	50 to 70' bgs	12,400 $\mu$ g/L decreased to 4,640 $\mu$ g/L Cr(VI), may show partial reduction signature; shallow well
MW-19 GMP	46 to 65' bgs	Avg. 960 μg/L Cr(VI), north of MW-20 bench, has increased somewhat in past two years; shallow well
MW-37D GMP	180 to 200' bgs	Avg. 1,400 μg/L Cr(VI), beneath Bat Cave Wash downgradient from MW-38; deep well
Plume: Floodplain Deposits		
MW-39-70 GMP	60 to 70' bgs	$6,640 \mu g/L Cr(VI)$ decreased to 200 $\mu g/L$ , decrease in concentration could be combination of dilution plus reduction, decrease in ORP values observed. Will sample MW-39-60 as contingency, to be analyzed if that well is above DL.
MW-34-100 GMP	88 to 98' bgs	350 to 880 μg/L Cr(VI)

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#### TABLE 2

Chromium Isotope Study – Potential Sample Locations, Phase II (to be determined following analysis of Phase I data) Chromium Isotope Study Workplan

Location, Sampling Plan	Depth Interval	Comments
California Background		
CW-03M	Intermediate Depth Well	Avg. 7.9 μg/L Cr(VI), alluvial fan deposits.
CW-04M	Intermediate Depth Well	Avg. 11.5 $\mu$ g/L Cr(VI), alluvial fan deposits.
MW-15	Shallow Depth Well	Avg. 10.7 μg/L Cr(VI), alluvial fan deposits.
Needles MW-11	Well depth of 280' (screened interval unknown)	Avg. 2.3 $\mu$ g/L Cr(VI), Needles Municipal Well. Oxygen and Deuterium isotope data suggest this is a fluvial well with a strong river water signature.
Tayloe	360 to 400' bgs	Avg. 0.5 $\mu$ g/L Cr(VI); may be too low to sample.
Arizona Background		
ADOT New Well	330 to 530' bgs	Avg. 8.5 µg/L Cr(VI), screened in alluvium
EPNG-2	322 to 482' bgs	Avg. 8.7 μg/L Cr(VI), screened in alluvium
GSRV-2	205 to 245' bgs	Avg. 29.1 µg/L Cr(VI), AZ side of river, should be background and is upgradient of plume (if present on AZ side of river), ADEQ Topock GW Study will evaluate well completion details with downhole survey scheduled for Oct. 2005, screened in alluvium
GSWC-1	Well depth of 250' (screened interval unknown)	Avg. 12.8 μg/L Cr(VI), expected to be screened in alluvium (no log available)
GSWC-2	Well depth of 500' (screened interval unknown)	Avg. 4.5 μg/L Cr(VI), screened in alluvium
GSWC-4	352 to 522' bgs	Avg. 10.1 μg/L Cr(VI), screened in alluvium
Langmaack	Well depth of 240' (screened interval unknown)	Avg. 21.4 µg/L Cr(VI), AZ side of river, should be background and is upgradient of plume (if present on AZ side of river), expected to be screened in alluvium (no log available)
TMLP-2	750 to 880' bgs	Avg. 16.0 μg/L Cr(VI), monitoring well.
Topock-2	100 to 140' bgs	Avg. 6.2 μg/L Cr(VI); east of Topock Marina; used as supply for compressor station and for municipal Topock, AZ
Topock-3	65' of screen in 150' of well	Avg. 9.2 μg/L Cr(VI); east of Topock Marina; used as supply for compressor station and for municipal Topock, AZ

#### TABLE 2

Chromium Isotope Study – Potential Sample Locations, Phase II (to be determined following analysis of Phase I data) Chromium Isotope Study Workplan

Location, Sampling Plan	Depth Interval	Comments
Plume Margin Wells (all are alluvial f	an wells unless other	wise stated)
MW-23	Bedrock Well	Bedrock Well between river and Compressor Station; has intermittent detectable Cr(VI) between 7 and 11 $\mu$ g/L.
MW-33-150	Deep Well	Avg. 4.0 μg/L Cr(VI)
MW-41M	Intermediate Depth Well	Avg. 6.1 μg/L Cr(VI)
MW-41S	Shallow Well	Avg. 13.8 μg/L Cr(VI)
Plume: Alluvial Fan Deposits		
MW-9	Shallow Well	Avg. 343 μg/L Cr(VI)
MW-11	Shallow Well	Avg. 635 μg/L Cr(VI)
MW-12	Shallow Well	Avg. 908 μg/L Cr(VI)
MW-20-100	Intermediate Depth Well	Avg. 3,970 μg/L Cr(VI)
MW-20-130	Deep Well	Avg. 6,920 μg/L Cr(VI)
MW-24A	Shallow Well	Avg. 3,200 μg/L Cr(VI)
MW-26	Shallow Well	Avg. 2,870 μg/L Cr(VI)
MW-31-60	Shallow Well	Avg. 3,380 μg/L Cr(VI); more recently 1,300 μg/L
MW-31-135	Deep Well	Avg. 275 μg/L Cr(VI)
MW-38D	Deep Well	Avg. 142 μg/L Cr(VI)
MW-39-80	Deep Well	Avg. 5,360 μg/L Cr(VI); more recently 1,420 μg/L
MW-39-10	Deep Well	Avg. 7,800 μg/L Cr(VI); more recently 4,500 μg/L
MW-40D	Deep Well	Avg. 33.3 μg/L Cr(VI); more recently 89.9 μg/L
TW-1	Screened across alluvial aquifer thickness	Avg. 4,680 μg/L Cr(VI)
TW-2S	Shallow Well	Avg. 5,950 μg/L Cr(VI); more recently 3,360 μg/L
TW-2D	Deep Well	Avg. 5,890 μg/L Cr(VI); more recently 2,180 μg/L
Plume: Floodplain Deposits		
MW-36-90	Deep Well	Avg. 1,450 $\mu$ g/L Cr(VI); more recently 72 $\mu$ g/L
MW-36-100	Deep Well	Avg. 1,410 $\mu$ g/L Cr(VI); more recently 307 $\mu$ g/L
MW-39-060	Intermediate Depth Well	3,590 $\mu$ g/L Cr(VI) decreased to 7 $\mu$ g/L, decrease in concentration could be combination of dilution plus reduction, decrease in ORP values observed. Will analyze only if Cr(VI) is still above DL.

Parameter	Analytical Method
Alkalinity	EPA 310.1
Ammonia	EPA 350.3
Boron	SW6010B/SW7000 series
Calcium	SW6010B/SW7000 series
Chloride	EPA 300
Fluoride	EPA 300
Iron, total	SW6010B/SW7000 series
Magnesium	SW6010B/SW7000 series
Manganese	SW6010B/SW7000 series
Nitrate	EPA 300
pH (lab/field)	EPA 150.1/SW9040
Potassium	SW6010B/SW7000 series
Silica	SW6010B/SW7000 series
Sulfate	EPA 300.0
Sodium	SW6010B/SW7000 series
Specific Conductance (lab/field)	EPA 120.1/SW9050
Sulfide	EPA 376.1
Total dissolved solids	EPA 160.1
Total Kjeldahl nitrogen	EPA 351.4
Total organic carbon	EPA 415.1 / SM 5310 B-D
<sup>2</sup> H	Laboratory SOP (continuous flow isotope ratio mass spectrometry [CF-IRMS])
<sup>18</sup> O	Laboratory SOP (continuous flow isotope ratio mass spectrometry [CF-IRMS])

# TABLE 3 Analytical Methods to be Used for General Chemistry Parameters Chromium Isotope Study Workplan

#### Notes:

 $\rm SM$  = Standard Methods;  $\rm SW$  = SW846 Update III EPA – EPA 600 Series for Chemical Analysis of Water and Wastes

# TABLE 4Project Implementation ScheduleChromium Isotope Study Workplan

Activity	Duration
Collect samples from Phase 1 wells	5 days. Currently, this is anticipated to occur the first week in May 2006. This week coincides with the GMP quarterly sampling event and the GBS bi-monthly sampling event.
Sample analysis and validation from Phase 1 sampling	3 weeks
Initial data evaluation. Following completion of this step, preliminary results will be presented to the TWG with the objective of recommending whether a second phase of sampling is warranted.	4 weeks
Optional: Collect samples from Phase 2 wells	5 days. This sampling event would be coordinated with other sampling events at the Topock site.
Optional: Sample analysis and validation from Phase 2 sampling	3 weeks
Data evaluation. Following completion of this step, preliminary results will be presented to the TWG presenting conclusions of the study and an outline of the report.	5 weeks
Complete report of findings.	7 weeks

Figures



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