Use of mineral/solution equilibrium calculations to assess the potential for carnotite precipitation from groundwater in the Texas Panhandle, USA

Anthony J. Ranalli [a, *], Douglas B. Yager [b]

[a] *Navarro Research and Engineering, Inc., 11025 Dover Street, Suite 1000, Westminster, CO 80021, USA*
[b] *U.S. Geological Survey, Central Mineral and Environmental Resources Science Center, Denver Federal Center, Box 25046, MS 973, Denver, CO 80225, USA*

ABSTRACT

This study investigated the potential for the uranium mineral carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$) to precipitate from evaporating groundwater in the Texas Panhandle region of the United States. The evolution of groundwater chemistry during evaporation was modeled with the USGS geochemical code PHREEQC using water-quality data from 100 groundwater wells downloaded from the USGS National Water Information System (NWIS) database. While most modeled groundwater compositions precipitated calcite upon evaporation, not all groundwater became saturated with respect to carnotite with the system open to CO_2. Thus, the formation of calcite is not a necessary condition for carnotite to form. Rather, the determining factor in achieving carnotite saturation was the evolution of groundwater chemistry during evaporation following calcite precipitation. Modeling in this study showed that if the initial major-ion groundwater composition was dominated by calcium-magnesium-sulfate (>70 precent Ca + Mg and >50 percent SO_4 + Cl) or calcium-magnesium-bicarbonate (>70 percent Ca + Mg and <70 percent HCO_3 + CO_3) and following the precipitation of calcite, the concentration of calcium was greater than the carbonate alkalinity ($2mCa^{+2} > mHCO_3^- + 2mCO_3^{-2}$) carnotite saturation was achieved. If, however, the initial major-ion groundwater composition is sodium-bicarbonate (varying amounts of Na, 40—100 percent Na), calcium-sodium-sulfate, or calcium-magnesium-bicarbonate composition (>70 percent HCO_3 + CO_3) and following the precipitation of calcite, the concentration of calcium was less than the carbonate alkalinity ($2mCa^{+2} < mHCO_3^- + 2mCO_3^{-2}$) carnotite saturation was not achieved. In systems open to CO_2, carnotite saturation occurred in most samples in evaporation amounts ranging from 95 percent to 99 percent with the partial pressure of CO_2 ranging from $10^{-3.5}$ to $10^{-2.5}$ atm. Carnotite saturation occurred in a few samples in evaporation amounts ranging from 98 percent to 99 percent with the partial pressure of CO_2 equal to $10^{-2.0}$ atm. Carnotite saturation did not occur in any groundwater with the system closed to CO_2.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The sustainability of nuclear energy, which provides 19 percent of electricity in the United States, relies upon a secure supply of uranium that can be produced in an environmentally acceptable manner. The last full assessment for uranium in the U.S., the Department of Energy's (DOE) National Uranium Resource Evaluation (NURE) program, was concluded in 1980. There has never

been an evaluation of the environmental vulnerabilities associated with mining these resources. Since NURE, resource reporting responsibilities have been split between DOE (reserves) and USGS (undiscovered resources). Neither agency has prioritized updates to uranium resources. Subsequently within the past 2 years both reserve and undiscovered resource estimates for the U.S. have been withdrawn from international reporting because they cannot be validated. As a result, the Energy and Minerals Mission Areas of the USGS are working to produce updated and scientifically defensible resource assessments based on current knowledge, to consider potential new sources of uranium resources, to aid DOE in updating their reserve estimates, and to measure the environmental

vulnerabilities associated with U resource development.

One potential new source of uranium in the United States is calcrete deposits of the mineral carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$), which forms at the surface in association with calcrete and has been identified in economic deposits in the Namib Desert of South West Africa and in Western Australia (Carlisle, 1978). Lesser deposits are also known in Tanzania, Jordan, Somalia, and Argentina. Calcrete is a term that was first proposed by Lamplugh (1902) to describe calcareous-cemented surficial deposits. The term has since been used to define calcareous deposition in pedogenic (caliche) and non-pedogenic environments (Mann and Horwitz, 1979). Calcrete, composed of calcium or calcium-magnesium carbonate, forms crudely lenticular masses up to tens of meters thick, several hundred meters to a few kilometers wide, and tens of kilometers in length. Calcrete deposits occupy the axial portions of paleostreams or existing drainage systems (Carlisle, 1978). Calcrete deposits can occur as perched, stratiform deposits that represent fossil groundwater that was saturated with respect to calcite. The non-pedogenic calcrete deposits that are the likely type of interest in the study area are stratiform to wedge-shaped and can be preserved as surficial mounds (Mann and Horwitz, 1979). Calcrete may form at or below the groundwater table where salinities are high and saturation of calcite occurs.

Known carnotite deposits are associated with calcrete deposits and form via evaporation of shallow, oxidizing, U and V-bearing groundwater in the capillary fringe along the axes of large stable drainages with low gradients and arid climates (Carlisle, 1983). Since carnotite forms near the surface, it is relatively easy to mine either by in-situ leaching or conventional open pit mining methods.

One of the tasks of the Integrated USGS Uranium Resource and Environmental Assessment Project is to determine the potential for formation of carnotite-hosted deposits in the United States. The Texas Panhandle region (Fig. 1) was selected for initial investigation based in elevated concentrations of U (20–500 ppm) in calcrete and calcareous lacustrine samples (Brad Van Gosen, USGS, oral communication, 2016), and the occurrence of elevated concentrations of dissolved vanadium (20–150 ppb) and U (2–30 ppb) in groundwater (Reedy et al, 2011). Climate conditions in the study area, while variable during the Quaternary, may have been or are currently favorable for carnotite formation because evapotranspiration is greater than precipitation and is conducive to concentrating trace elements in upwelling groundwater.

1.1. Purpose and scope

The purpose of this paper is to use the results of mineral-solution equilibrium modeling of groundwater in the Texas Panhandle to:

1. Determine the effectiveness of evaporative concentration to precipitate carnotite from modern groundwater in the Texas Panhandle.
2. Develop a conceptual model of carnotite formation that may lead to the discovery of carnotite in areas other than Namiba and Western Australia.

2. Methods

The potential for precipitation of carnotite in the Texas Panhandle region was assessed by calculating the degree of saturation of carnotite as a function of increasing uranium concentration in groundwater and evaporation of groundwater. Calculations were performed using the USGS computer software code PHREEQC (Parkhurst and Appelo, 1999; http://wwwbrr.cr.usgs.gov/projetcs/GWC_coupled/phreeqc/). Groundwater-quality data were

retrieved from the USGS NWIS database for 100 groundwater wells screened in the Ogallala aquifer in the Texas Panhandle region (Fig. 1). Data for these wells are presented in Supplementary Table 1 and were accessed in April 2014 at http://waterdata.usgs.gov/tx/nwis/qw.

2.1. Geochemical modeling

The groundwater well data were retrieved from an area bounded on the north at $36°00'00''$, on the south at $32°00'00''$, on the west at $-104°15'00''$, and on the east at $-100°00'00''$. The Ogallala aquifer is the major producing aquifer in the Texas Panhandle (Fig. 1). Suitability of these data for the inclusion into PHREEQC was assessed by calculating a cation/anion balance for each sample, which ranged from -4.63 percent to 7.20 percent, therefore all samples were considered sufficiently accurate for modeling purposes. The ionic strength of the groundwater in this data set ranged from 0.01 to 0.07, therefore, the minteq.v4.dat database was used, which contains thermodynamic data for carnotite and uses the Davies equation (Langmuir, 1997) for the calculation of activity coefficients for dissolved ions and is valid up to ionic strengths of 0.5 molal. The carbonate complexes $CaUO_2(CO_3)_3^{-2}$, $Ca_2UO_2(CO_3)_3$, and $MgUO_2(CO_3)_3^{-2}$ were not included in the minteq.v4.dat database but were identified as dominate U(VI) aqueous species in groundwater by Curtis et al., (2006). Thermodynamic data for these complexes were provided to the authors by Gary Curtis (USGS Water Mission Area) and were added to PHREEQC. Evaporative concentration factors of 2-fold (50 percent of the water is evaporated), 5-fold (80 percent of the water is evaporated), 10-fold (90 percent of the water is evaporated), 15-fold (93 percent of the water is evaporated), 20-fold (95 percent of the water is evaporated), and 100-fold (99 percent of the water is evaporated) at partial pressures of CO_2 at $10^{-3.5}$, $10^{-3.0}$, $10^{-2.5}$, and $10^{-2.0}$ atm under open and closed conditions were used. In all of these evaporation scenarios only 4 of 100 wells exceeded an ionic strength of 0.5 upon evaporation to 99 percent and were not used in this evaluation.

The dissolution of carnotite as written in the PHREEQC minteq.v4.dat database is:

$$KUO_2VO_4 + 4H^+ = K^+ + UO_2^{+2} + VO_2^+ + 2H_2O \qquad (1)$$

From this equation the saturation index (SI) reflecting the degree of saturation of the groundwater with respect to carnotite can be written as:

$$SI_{carnotite} = aK^+ aUO_2^{2+} aVO_2^+ / a[H^+]^4 K_{carnotite} \qquad (2)$$

where a = activity and $K_{carnotite}$ = the equilibrium constant for reaction 1. Therefore, for carnotite to form, the concentration, or more accurately the activity, of K^+, UO_2^{+2}, and VO_2^+ must be sufficiently great to produce carnotite.

Given that the ionic strength of all groundwater samples was less than 0.5 molal, even upon evaporation amounts of 98 percent, we felt the minteq.v4.dat database, with the addition of the carbonate complex thermodynamic data provided by Gary Curtis (USGS), was adequate. However, to test the validity of the thermodynamic data used, selected samples were also analyzed with the llnl.dat database. For samples that achieved saturation with respect to carnotite the saturation indices calculated with the llnl.dat database were more negative than those calculated with the minteq.v4.dat database for the lower evaporation amounts but at the higher evaporation amounts, 94 percent and greater, the saturation indices calculated with both databases were the same. For samples that did not achieve saturation with respect to carnotite the saturation indices calculated with the llnl.dat