

Fe-OXIDES IN ASH FLOW TUFF: ADSORPTION AGENT FOR CARBON DIOXIDE ?

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ABSTRACT

During the ongoing studies to site a high level radioactive waste repository in the United States, the question of potential release and retardation of carbon-14 as gaseous CO₂ has arisen. Carbon-14 is generated by neutron interaction with either nitrogen or oxygen in and around spent fuel rods. If the fuel rod canisters are breached, atmospheric oxygen can interact with the carbon to produce radioactive CO₂. Because such potential gaseous releases could adversely affect the performance of a repository, three media were investigated as retardation mechanisms to slow CO₂. Of the media involved (gas, liquid, solid), this paper focuses on Fe-oxides in ash flow tuffs as a potential retardant of CO₂.

Previous studies of the fluid media in a deep, mined geologic repository as retarding agents have indicated the following results. Gaseous isotopic exchange of carbon-14 for carbon-12 is at equilibrium and therefore provides no retention mechanism for the radioactive species. Liquid retardation is dominated by bicarbonate equilibria, which can retard radioactive CO₂ by a factor of approximately 30 to 90. Site-specific conditions at the potential repository at Yucca Mountain then suggest that carbon-14 releases above regulatory values could then occur.

This review paper incorporates studies of minerals that adsorb CO₂ with specific data from ash flow tuffs at Yucca Mountain to determine if in-situ Fe-oxides could sufficiently increase CO₂ travel times to the surface beyond the regulatory period of concern. Experimental studies have shown that goethite (FeOOH) has the ability to retard (by adsorption) CO₂ travel times by an order of magnitude greater than bicarbonate equilibria alone. Ash flow tuffs at Yucca Mountain contain 1 to 2 weight percent (wt.%) hematite (Fe₂O₃), primarily as lath shaped, micron to sub-micron grains. Interaction of this oxide with warm water would react to form goethite. Such waters would come from the thermal pulse initiated by emplacement of hot radioactive waste containers at Yucca Mountain. One can assume that a 50% transformation of hematite to goethite is reasonable.

An amount of 0.5 to 1.0 wt.% fine grained goethite would calculate to a surface area of 0.029 to 0.29 m² per cm³ of rock for CO₂ adsorption. Yucca Mountain geochemical data supports calculations of 7.9 x 10⁻⁷ moles of CO₂ per m² of goethite surface area. Therefore, one can expect an additional adsorption of CO₂ by Fe-oxides in ash flows at Yucca Mountain of 2.2 x 10⁻⁷ to 2.2 x 10⁻⁸ moles per cm³ rock. Final calculations of retardation factors for the complete system will range from 160 to 240, thereby retaining radioactive CO₂ within the undisturbed potential repository at Yucca Mountain well beyond the period of regulatory concern.

INTRODUCTION

Research by the Department of Energy (DOE) has indicated that carbon-14 (C-14) may be released from spent fuel containers after emplacement in a high-level waste (HLW) repository. The most plausible production mechanism of C-14 is neutron interaction with either nitrogen impurities in the uranium fuel or oxygen in films on surfaces of the fuel rod cladding (1). The latter process leaves C-14 readily available on the cladding surfaces for release. Introduction of atmospheric oxygen into the canisters will react with C-14 to form carbon dioxide (CO₂). Unrestricted gaseous transport of CO₂ in unsaturated ash flow tuffs could allow the full inventory of C-14 to be released during the 10,000-year assessment period for a proposed HLW repository.

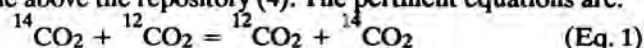
During the last ten years, a controversy has arisen as to whether any natural mechanisms would retard radioactive CO₂ to a degree suitable for repository requirements. Most of the retardation studies have focussed on C-14 interaction with gaseous and liquid phases in the surrounding rocks. The studies suggest that C-14 travel time to the surface as gaseous CO₂ would be much less than the time of regulatory concern of 10,000 years (2). Retardation studies involving minerals in ash flow tuffs seem incomplete, in that site specific data from Yucca Mountain was often neglected. The author has there-

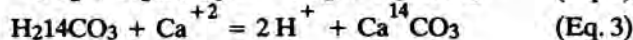
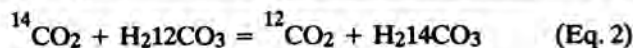
fore decided to synthesize the available data on the affects of CO₂ retardation in geologic media and incorporate the most accurate data on Yucca Mountain ash flow tuffs known to him. The objectives of the present study are two fold: to determine if there is evidence of substantial retardation factors created by certain mineral phases in the geologic media of the proposed repository and if the mineral phases are present in sufficient abundance.

PREVIOUS WORK

Past studies have focussed primarily on retardation mechanisms for C-14 in gas and liquid media in ash flow tuffs (1,3). Research has indicated that exchange of C-14 for C-12 in the gaseous state (CO₂) provides little if any retardation of the isotope in question. First, the inventory of gaseous CO₂ available for exchange in the rock is quite small. Second, the re-equilibration of the two carbon isotopes in an advective system with atmospheric gas is constant and therefore provides almost no retardation of C-14.

Retardation mechanisms in the liquid state were found to be dominated by bicarbonate equilibria in the unsaturated zone above the repository (4). The pertinent equations are:





The set of equations assumed that the bicarbonate solution equilibria was established as a function of calcium concentration, equilibrium of the liquid with calcite and the prevailing partial pressure of carbon dioxide (4). Calculations of liquid phase retardation factors (RF) for CO_2 in unsaturated ash flow tuffs at Yucca Mountain produced values from 30 to 88. A nominal value of 30 would allow excess C-14 to escape to the unrestricted environment in 3000 years.

Experimental work on mineral phase retardation (5) consisting of passing CO_2 gas through alluvial sediment samples determined that the gas was retarded by a factor of 8.1 to 17.4 (Table I) over that of the bicarbonate equilibria retardation value. With a nominal value of 10, the geologic retardation value would be 10 times the bicarbonate RF ($= 10 \times 30 = 300$). Striegl and Armstrong (5) note that the lack of change in isotopic composition indicates a capacity for carbon dioxide retention beyond that contained in the pore water alone (Fig. 1). The authors of this work suggested that the enhanced retardation was created by CO_2 adsorption on the surface of Fe-oxides, a finding previously suggested by Reardon, et al (6).

This theory was further substantiated by experimental

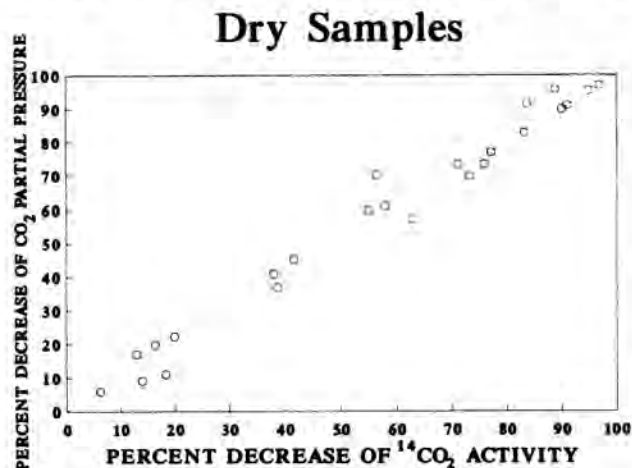


Fig. 1. Percent of decrease of PCO_2 versus percent decrease of $^{14}\text{CO}_2$ activity for dry experiments. Note that the lack of change in isotopic compositions suggests that there is a capacity in the soils for carbon dioxide retention beyond that contained in the pore water alone. Values from Striegl and Armstrong (1990).

work that determined that the Fe-oxide that adsorbed CO_2 in substantial amounts was goethite (FeOOH) (7). Partition coefficients of goethite for CO_2 dissolved in liquid at appropriate pH and ionic strength conditions for unsaturated tuffs of the southwest United States range from approximately 100 to 400 (Fig. 2). These partition coefficients for goethite are wholly consistent with the retardation factors given by Striegl and Armstrong (5) for CO_2 in geologic media.

DISCUSSION

Once Fe-oxides were determined to adsorb CO_2 and retard the gas in geologic media, the next questions must focus on HLW repository site-specific criteria. Four questions are

TABLE I
 CO_2 Retardation Factors (RF) In Recent Sediments

| | Peoria | Radnor | Toulon |
|------------------------|--------|--------|--------|
| CO_2 - ret | 4.77 | 27.9 | 3.69 |
| DIC | 0.59 | 1.60 | 0.33 |
| CO_2 -r / DIC | 8.1 | 17.4 | 11.20 |

Striegl and Armstrong (1990)

The pH and Ionic Strength Dependence of Carbonate Adsorption

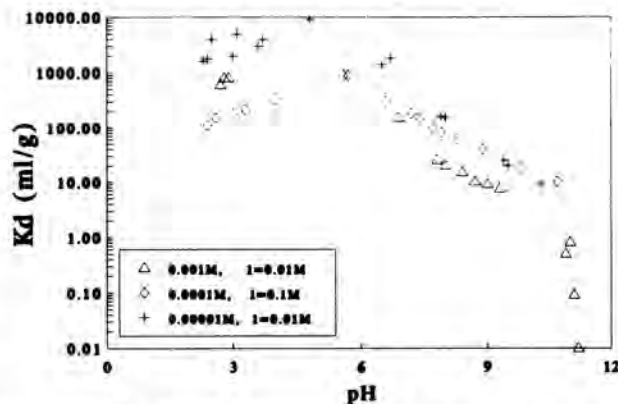


Fig. 2. The pH and ionic strength dependence of carbonate adsorption on goethite. Notice that for water in unsaturated tuffs at Yucca Mountain, pH values range from 6.9 to 7.4. That suggests that K_d values would vary from approximately 100 to 400. Figure data from Rundberg and Albinsson (1991).

considered for the ash flow tuffs of Yucca Mountain, the potential site for a repository. One, are Fe-oxides present in tuffs and what is the morphology of the phases? Two, if Fe-oxides are present, is there a sufficient quantity of Fe-oxides to serve as effective adsorbing agents for radioactive CO_2 ? Three, is the Fe-oxide chemistry correct to get maximum retardation of CO_2 ? Four, are there special effects produced by the repository that may alter the chemistry of the Fe-oxides present in the tuffs?

Ash flow tuffs are now recognized to produce very fine grained, rod shaped, hematite (Fe_2O_3) after emplacement (8). These lath-shaped crystals range in size from 20×140 nm in basal flows to 120×800 nm in interior sections of the flows. The differing sizes are dependent on the cooling rates of those portions of the flows. Such small, lath-shaped Fe-oxide crystals could provide large surface areas for adsorption of gases in ash flow tuffs.

The second question to be resolved about the tuffs at Yucca Mountain is the amount of Fe-oxides present. Mineralogic characterization work at Los Alamos National Laboratory has determined that the amount of Fe-oxides in Yucca Mountain ash flow tuffs ranges from 1 to 2 weight percent and is composed predominantly of fine-grained hematite (9). Therefore, one can conclude that there is a sizable quantity of Fe-oxide present in the Yucca Mountain tuffs. Hematite of these dimensions and weight percents provide a large surface area (0.29 to 2.9 m^2 per cm^3 rock, respectively) for CO_2

adsorption. However, the most abundant Fe-oxide at Yucca Mountain is hematite, not the more desirable phase for CO₂ adsorption, goethite.

If the alteration of hematite to goethite is both plausible and probable, then an effective retardation mechanism for C-14 could exist in the ash flows at Yucca Mountain which surround a potential HLW repository. Hematite alters to goethite with the addition of water, as shown by the following equation:



The oxidation mechanism of Fe-oxides in ash flow tuffs is rather poorly understood. However, from corrosion studies of metal alloys and observation of Fe-oxides in basalts, oxidation is shown to be dependent on grain size, trace elements (Mg, Ti, Mn), Eh, pH, temperature of reaction and H₂O saturation (10). In the case of the fine-grained hematite grains present in Yucca Mountain tuffs, most of the parameters are favorable for oxidation of hematite to goethite in the presence of warm (90 - 110°C) water.

Warm water will probably invade many portions of ash flows in the vadose zone when the thermally hot radioactive fuel rods are emplaced in the repository. Such hot radioactive waste will drive surrounding water away from the canisters (11), creating a thermal pulse which will allow the hematite to oxidize to goethite. Such a chemical reaction provided by a thermal pulse will produce an abundance of fine-grained goethite in the ash flows which can then retard the escape of radioactive CO₂.

A natural analog to a HLW thermal pulse is represented by the vapor phase zone containing oxidized hematite directly above the vitrophyre in the Topopah Springs Member at Yucca Mountain (12). The silicic ash that formed the vitrophyre was emplaced at high enough temperatures to sinter the ash particles directly back to glass and retained all magmatic volatiles. Upon cooling of the vitrophyre, the water-rich gas was released to the overlying tuffs and created many alteration products. One of the chemical reactions consistently noted in such vapor phase alteration zones is the oxidation of hematite to goethite (9,12).

If one then compiles site specific data for Yucca Mountain and uses certain basic assumptions, a realistic range of RF's could be calculated for gaseous CO₂. The primary assumption is that of how much hematite can be transformed to goethite in the ash flows of Yucca Mountain. A thermal pulse that transforms 50 percent of primary hematite to goethite would equate to 0.5 to 1.0 weight percent hydrated Fe-oxide in ash flows above the repository site at Yucca Mountain. This would then translate to a surface area of 0.029 to 0.29 m² per cm³ rock goethite available for retardation of CO₂. Figure 2 indicates that the sorption isotherm for carbonate at pH 7 and an aqueous bicarbonate concentration of 0.0015 M (average water chemistry in Topopah Springs) gives a solid phase concentration of 7.9 x 10⁻⁷ moles of carbonate per m² of goethite surface area. Therefore the additional capacity due to Fe-oxide would range from 2.2 x 10⁻⁷ to 2.2 x 10⁻⁸ moles per cm³ rock. Finally, using the RF data of Striegl and Armstrong (5) and Rundberg and Albinsson (7), one can calculate a final range of RF values for Yucca Mountain tuffs from 160 to 240.

CONCLUSIONS

To summarize, the following items are now known about the Fe-oxides in ash flow tuffs which may cause effective

adsorption and retardation of radioactive CO₂ released from failed spent fuel canisters in a HLW repository. One, solid phases in geologic media can retard C-14 releases by an order of magnitude over that of liquid bicarbonate equilibria alone. Two, there are experimental results that indicate that an Fe-oxide, goethite, is the predominant phase that retards C-14. Three, there are abundant, fine-grained hematite grains dispersed throughout ash flow tuffs. Four, the alteration of hematite to goethite in unsaturated ash flow tuffs is accomplished by the addition of water at slightly elevated temperatures. Five, a thermal pulse from hot spent fuel canisters would push warm water away from the canisters and be available to alter hematite to goethite. Six, an abundance of fine-grained goethite with high surface areas in ash flow tuffs would provide high adsorption capabilities for C-14 in the form of gaseous CO₂.

ACKNOWLEDGEMENTS

This review paper was written to synthesize data currently available on carbon-14. It is not intended to provide a detailed estimate of CO₂ retardation values at Yucca Mountain. This author assumes all responsibility for the analysis and conclusions in this report, which do not necessarily represent those of the Environmental Protection Agency.

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REFERENCES

1. W.B.LIGHT, E.D.ZWAHLEN, T.H.PIGFORD, P.L.CHAMBRE, and W.W.L.LEE, "C-14 Release and Transport from a Nuclear Waste Repository in an Unsaturated Medium," LBL-28923, Lawrence Berkeley Laboratory (1990).
2. U. S. Environmental Protection Agency, "Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes", Code of Federal Regulations, 40 CFR 191.
3. B.ROSS, S.AMTER, N.LU, "Numerical Studies of Rock-Gas Flow at Yucca Mountain," SAND91-7034, prepared by Disposal Safety Incorporated for Sandia National Laboratory, (1991).
4. B.ROSS, "Gas-Phase Transport of Carbon-14 Released from Nuclear Waste into the Unsaturated Zone", *Scientific Basis for Nuclear Waste Management XI*, pp. 273-284, Materials Research Society, (1988).
5. R.G. STRIEGL and D.E. ARMSTRONG, "Carbon Dioxide Retention and Carbon Exchange on Unsaturated Quaternary Sediments," *Geochem. Cosmochem. Acta*, V54, pp. 2227-2283, (1990).
6. E.J. REARDON, R.D. KELLERMAN, R.W. GILLHAM, and H.M. JOHNSTON, "Carbonate Sorption Capacity of Iron Hydroxide and Soil Material", *CNS Int. Conf. on Radioactive Waste Management*, 7-11, Sept. 1986, Winnipeg (1986)
7. R.S.RUNDBERG and Y.ALBINSSON, "Carbonate Adsorption onto Goethite as a Function of pH and Ionic

- Strength," LA-UR -91-3244, Los Alamos National Laboratory, (1991).
8. C.M. SCHLINGER, R.J. ROSENBAUM, and D.R. VEBLER, "Fe Oxide Microcrystals in Welded Tuff from Southern Nevada: Origin of Remanence Carriers by Precipitation in Volcanic Glass," *Geology*, V16, pp.556-559, (1990).
 9. D.L. BISH and S. J. CHIPERA, " Revised Mineralogic Summary of Yucca Mountain, Nevada," LA-11497-MS, Los Alamos National Laboratory, (1989).
 10. S.E. HAGGERTY, " Oxidation of Opaque Mineral Oxides in Basalts" *Oxide Minerals*; in Reviews in Minerals, Ch 4, V3, Douglas Rumble (ED), Mineralogical Society of America (1976).
 11. U.S. Environmental Protection Agency "Release of C-14 in Gaseous Form from High-Level Waste Disposal" Science Advisory Board Radiation Advisory Committee on High Level Waste/ Carbon-14,(1992).
 12. F.A. CAPORUSCIO, D. VANIMAN, D.L. BISH, D. BROXTON, B. ARNEY, G. HEIKEN, F. BYERS, R. GOOLEY, R. SEMARGE, " Petrologic Studies of Core from Drill Hole USW-G2 and of the Lower Crater Flat Tuff in Core from Drill Hole Ue25B1H, Yucca Mountain, Nevada," LA-9255-MS, Los Alamos National Laboratory (1982).