PROCEEDINGS, Eleventh Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 21-23, 1986
SGP-TR-93

THERMAL STABILITY OF CHELATED INDIUM ACTIVABLE TRACERS

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ABSTRACT

The thermal stability of indium tracer chelated with organic ligands ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) was measured for reservoir temperatures of 150, 200, and 240°C. Measurements of the soluble indium concentration was made as a function of time by neutron activation analysis. From the data, approximate thermal decomposition rates were estimated. At 150°C, both chelated tracers were stable over the experimental period of 20 days. At 200°C, the InEDTA concentration remained constant for 16 days, after which the thermal decomposition occurred at a measured rate constant of $k_{obs} = 0.09\ d^{-1}$. The thermal decomposition of InNTA at 200°C showed a first order reaction with a measured rate constant of $k_{obs} = 0.16\ d^{-1}$. At 240°C, both indium chelated tracers showed rapid decomposition with rate constants greater than 1.8 d^{-1}. The data indicate that for geothermal reservoir with temperatures up to about 200°C, indium chelated tracers can be used effectively for transit times of at least 20 days. These experiments were run without reservoir rock media, and do not account for concomitant loss of indium tracer by adsorption processes.

INTRODUCTION

Reinjection of thermally spent geothermal brines is attractive for two distinct advantages. For environmental protection, it provides disposal of hazardous waste brines which cannot be discharged to surface waters. For operational efficiency, it serves to maintain reservoir pressure and enhance thermal energy recovery from the reservoir formation. However, uncertainties exist about the long-term potential of reinjection, such as the possibility of permeability reduction, inducement of seismic events, and the reduction of discharge enthalpy by initial breakthrough of cooled recharge fluid causing losses in steam production. To study these uncertainties, several tracer investigations have been performed to investigate reservoir structure and path networks (e.g., Horne, 1982). The features of tracer response important for these studies are early breakthrough time, peak tracer concentration, fractional recovery, and shape of retardation tail. Many tracers are not sufficiently sensitive for determining breakthrough time and retardation tail. Among the properties of suitable tracers for such studies, problems exist with thermal stability and adsorption processes leading to losses and retardation of the tracer with respect to the recharge fluid. Activable tracers are considered for their high sensitivity by radioactivity measurement and wide variety of stable materials compatible with the high-temperature and adsorption-prone geothermal reservoir environment. This paper discusses the selection of suitable activable tracers for liquid-dominated reservoirs and thermal stability of complexed activable tracers over a range of geothermal reservoir temperatures.

NEUTRON ACTIVATION ANALYSIS

The technique of neutron activation analysis is a unique combination of nuclear and chemical processes selected to optimize the precision and accuracy of trace-element chemical analysis or a high-dilution tracer study. Very few analytical methods offer the versatility and sensitivity achievable by neutron activation analysis. The advantages of neutron activation analysis and its application to ground water aquifers are described by Kruger (1971). For a tracer study a suitable stable material with proper chemical and nuclear properties must be selected so that upon thermal neutron irradiation it will produce the desired activation product. Irradiation with thermal neutrons is preferable because thermal neutron capture cross sections are large and production of interfering radioisotopes are minimized. Several devices are readily available with large thermal neutron fluxes, such as low-power nuclear research reactors and radioisotope sources. The quantity of tracer material needed as a geothermal reservoir tracer is dependent upon the neutron flux available. The higher the neutron flux the smaller the quantity of stable element required. The amount of the radioisotope produced at the end of irradiation period is proportional to the parent isotope and its disintegration rate is given by the radioactivation equation:

$$D_0 = n\,\sigma\,\varphi\,(1-e^{-\lambda\tau}) \tag{1}$$

where, D_0 ≡ amount of radioactivity of the product radionuclide at the end of irradiation (disintegrations per second, dps); φ = incident neutron flux (n/cm^2 sec); σ = neutron capture cross section (cm^2); n = number of atoms present in the sample which can give rise to the product activity; λ = decay constant of the product radionuclide (sec^{-1}); and τ = length of irradiation (sec).

After the end of irradiation, the activity of the product radionuclide decreases according to the radioactivity decay law:

$$D_t = D_0\,e^{-\lambda t} \tag{2}$$

where, t = the elapsed time from the end of irradiation to the start of measurement; D_t = amount of radioactivity of the product radionuclide at time t.

The minimum amount of a tracer element required for efficient detection under given irradiation and counting conditions is given by the sensitivity equation:

$$w_{\min} = \frac{N_{\min} M}{\varepsilon \, \sigma \, \varphi \, A' \, f \, (1 - e^{-\lambda \tau}) \, e^{-\lambda t}} \tag{3}$$

where, $w_{\min}$ = minimum weight of target element (grams); f = fractional isotopic abundance; A' = Avogadro's number; M = atomic weight of the element; $\varepsilon = N/D$, counting efficiency; and $N_{\min}$ = minimum number of counts during counting time interval (cps). Other parameters, such as chemical yield if chemical separations are required, can be included in the sensitivity equation. For similar irradiation and measurement conditions of the tracer and a known standard, the activable tracer measurement reduces to the simple form of:

$$w_{tr} = w_{std} \frac{D_{tr}}{D_{std}} \tag{4}$$

where the subscripts *tr* and *std* indicate tracer and standard respectively.

The irradiation duration is a relative parameter and depends upon the nuclear properties of the selected isotopic tracer as well as on the design characteristics of the activation analysis. When tracer concentrations are close to the limits of sensitivity, it is desirable to irradiate enough time for the tracer to approach a level of steady state or saturation, in which radioactive products disintegrate at the same rate at which they are formed. If the irradiation is terminated before the steady state is achieved, then the disintegration rate of the active nuclide is less than its rate of formation. For short-lived active nuclides the approach to saturation activity level is fast. On the other hand, for long-lived nuclides a careful estimation of the minimum desired level of radioactivity reduces the time period of the activation process.

The radioactivity of the tracer is measured by monitoring selectively the energies and intensities of the gamma-rays emitted by the product radionuclide with a radiation detector coupled with a multichannel analyzer system. Several radiation detectors are commercially available but the sodium-iodide thalium, NaI(Tl), detectors are most useful when sensitivity is the main concern or low levels of radioactivity are to be measured (Friedlander et al., 1981).

Occasionally, samples may contain major constituents whose activation would lead to high levels of radiation or to generation of radionuclides with gamma radiation interfering with the radiations from the product nuclide. These samples require chemical preconcentration of the trace elements prior to neutron activation. Several techniques are available for separation of the interfering constituents; however, the most favorable is the rapid ion exchange separation technique (Matthews and Riley, 1970). If ion exchange is not applicable, an alternative preconcentration method is coprecipitation (Navada et al., 1981; Drabaek, 1982). Postirradiation separation is necessary when the highest possible sensitivity is required. Postirradiation separations are more reliable because once the radioactive species are produced any chemical manipulation can be performed on the sample without contamination of the radioelements being measured.

SELECTION OF ACTIVABLE TRACERS

The requirements for a suitable activable tracer are: (a) a background concentration as close as possible to the minimum detectable amount of tracer by available detection systems, (b) large natural isotopic abundance, (c) large neutron activation cross sections, (d) appropriate gamma radiation of the product radionuclide for measurement by gamma-ray spectrometry, and (e) optimum half-life of the product radionuclide.

An optimization analysis for external tracers, based on a literature survey on the chemical composition of geothermal effluents taking into account the criteria for activable tracer, was conducted and four potential activable tracers were identified: vanadium (V), cobalt (Co), indium (In), and dysprosium (Dy). Table 1 summarizes the sensitivity calculations of the elements based on 10-minute irradiation in thermal neutron flux of 2×10^{6} n/cm^{2}-sec and 30-minute delay time until measurement. The minimum value of N = 60 cpm at the measurement time was set as an additional sensitivity requirement. This arbitrary counting rate value is high enough to permit efficient detection of the gamma-ray of interest. Indium is considered to be the most promising of the four potential activable tracers, because of its unique combination of good detection sensitivity and relatively high energy of major gamma-ray emission. High-energy gamma-rays are preferred when interfering radionuclides with low gamma-energy are present because their Compton scattering contribution to the tracer full-energy peak is negligible. However, counting efficiency decreases with increasing gamma-ray energy.

Indium is a member of the Group IIIA elements of

Table 1. Laboratory Sensitivity for the Potential Activable Tracers

TARGET NUCLIDE

Element	Isotope	f^{*}	$\sigma_{(n,\gamma)}^{*}$
V	^{51}V	0.997	4.88
Co	^{59}Co	1.000	19
In	^{115}In	0.957	70
Dy	^{164}Dy	0.281	900

PRODUCT NUCLIDE

Isotope	$T_{1/2}^{*}$	Major-γ (MeV)*	Sensitivity (ng)
^{52}V	3.75 m	1.434	126.06
^{60m}Co	10.47 m	0.059	2.24
^{116m}In	54.12 m	1.294	0.59
^{165}Dy	2.33 h	0.095	0.10

* The nuclear data have been adapted from Lederer and Shirley (1978). f = isotopic abundance; $\sigma_{(n,\gamma)}$ = thermal neutron cross section in barns.

the Periodic table, and has only two naturally occurring isotopes with mass numbers 113 and 115. The cross sections for $^{113}_{49}\mathrm{In}(n,\gamma)^{114}_{49}\mathrm{In}$ and $^{113}_{49}\mathrm{In}(n,\gamma)^{114m}_{49}\mathrm{In}$ reactions are relatively small, 3 and 5 barns respectively. Also, $^{114}\mathrm{In}$ has a relatively short half-life (71.9 seconds), while $^{114m}\mathrm{In}$ has a half-life of 49.5 days which is very long for an activable tracer. In addition to these unfavorable properties, $^{113}\mathrm{In}$ has a small isotopic abundance (4.3%); therefore, this natural isotope of indium is not useful for geothermal tracing. On the other hand, the cross sections for $^{115}_{49}\mathrm{In}(n,\gamma)^{116}_{49}\mathrm{In}$ and $^{115}_{49}\mathrm{In}(n,\gamma)^{116m}_{49}\mathrm{In}$ reactions are quite large, 41 and 70 barns respectively. The 14.1 second $^{116}\mathrm{In}$ is easily excluded from any tracing applications because of its extremely short half-life. The unique combination of good isotopic abundance of $^{115}_{49}\mathrm{In}$ (95.7%) and the fairly good half-life of its activation product (54.12 minute-$^{116m}\mathrm{In}$) is the chief reason that makes indium an excellent activable tracer. The gamma-ray spectrum of this isotope consists of several gamma rays ranging from 0.138 to 2.225 MeV. Its major gamma ray is 1.2935 MeV with an absolute intensity of 85 percent, which makes its detection tractable by scintillation detectors.

Indium is a relatively rare metal and is widely distributed in combined form. The metal occurs in minerals either as an isomorphous replacement for other elements of similar ionic radii or as structural member of the principal mineral (Linn and Schmitt, 1972). The indium concentration of natural waters is very low. Hot spring waters in Bulgaria were reported to contain up to 40 ppb indium (Smith et al., 1978), while indium concentration in Pacific Ocean water was found to be 4 ppt (chow and Snyder, 1969). The exact indium concentration of any representative geothermal fluid has not been evaluated, however Cosner and Apps (1978) reported that the indium content of geofluids is less than 100 ppb.

Indium exhibits positive oxidation states from one through three, but the common valence is three. Since the use of a cation tracer is not advisable (Adams, 1985) and because anionic solute species tend to be more conservative than cationic species, chelation of indium is necessary to ensure chemical stability in geofluids.

The organic ligands ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) form strong water-soluble complexes with a variety of elements, and were chosen to enhance the solution stability of the selected tracer. Both chelating agents have the ability of ionizing each one of their carboxyl groups. In general, EDTA can form coordination bonds at six sites, the four oxygen and the two nitrogen sites. The metal complexes of EDTA form five five-membered rings and reduce the charge on the central atom by four. On the other hand, NTA can form coordination bonds at four sites, the three oxygen and one nitrogen sites. The metal complexes of NTA form three five-membered rings and reduce the charge of the central atom by three. The two indium chelates are similar but InEDTA possesses two additional rings. The stability constant for InEDTA is K_s =24.9 and for InNTA is K_s = 15.9. The principal factor influencing the stronger stability of InEDTA over InNTA is the extra number of rings, or more specifically the stability of the metal complex increases with increasing number of chelate rings (Dwyer and Mellor, 1964).

The thermal stability of the chelated tracers is an important consideration for their use in geothermal reservoirs. Venezky and Moniz (1969) reported that EDTA in aqueous solutions is stable up to 200°C. They observed a secondary degradation process at this temperature in which the decomposition products retain chelating ability. At higher temperatures primary degradation occurs forming products without evident chelating characteristics. Martell et al. (1975) reported that NTA does not cleave at temperatures up to 260°C but decomposes above 290° through a stepwise decarboxylation. Since the information available in the literature is based primarily on the free organic ligands, the thermal stability of indium chelated complexes in particular, required experimental determination.

EXPERIMENTAL

The study concentrated mainly on the laboratory investigations needed to provide a linkage between current information about indium chelated tracers and their unknown behavior in liquid-dominated geothermal systems. The experimental work consisted of two parts. First, batch experiments were carried out at room temperature to evaluate and compare the time stability of indium solubility as EDTA and NTA complexed ions. Second, thermal stability measurements of the indium chelates were performed for reservoir temperatures of 150, 200, and 240°C, to determine thermal decomposition rates from the experimental data.

Apparatus: Gold plated pressure vessels of approximately 40-ml volume, provided by the U.S. Geological Survey, Menlo Park, were employed for the high temperature experiments. The choice of gold plated pressure vessels was dictated by the desire to minimize interactions between tracer solution and vessel wall. The pressure vessels were housed in an airbath at constant temperature within ±0.5°C. The samples were activated in the Stanford Linear Accelerator Center (SLAC) $^{252}\mathrm{Cf}$ neutron irradiation source at a thermal neutron flux of $2\mathrm{x}10^6$ n cm^{-2} s^{-1}. Measurement of 54.12 minute-$^{116m}\mathrm{In}$ radioactivity was performed by gamma-ray NaI(Tl) scintillation spectroscopy with a multichannel analyzer in the Stanford Environmental Engineering laboratory.

Reagents: The indium standard solution was prepared by dissolving high-purity indium metal in concentrated HNO_3. The disodium salts of analytical reagent grade EDTA and NTA were used for the ligand standards. Milli-Q reagent grade deionized water was used as solvent. The indium solution was acidified to reduce adsorption onto container walls. The pH of the organic ligand standards was adjusted to a pH slightly above the last pK value of the corresponding ligand, because chelating agents are polyprotic acids and usually only the fully deprotonated form of the acid gives complexes with the metal ion. The indium tracer solutions were formed with a chelon to metal mole ratio of 10 to increase the stability of the indium-chelate complexes.

Procedure: The time stability experiments at room temperature (20-22°C) were conducted over a two month period. Stock solutions of indium chelated tracers at a concentration of 505 ppm were prepared and stored in glass containers with ground glass stoppers. At regular intervals two 5-ml samples of

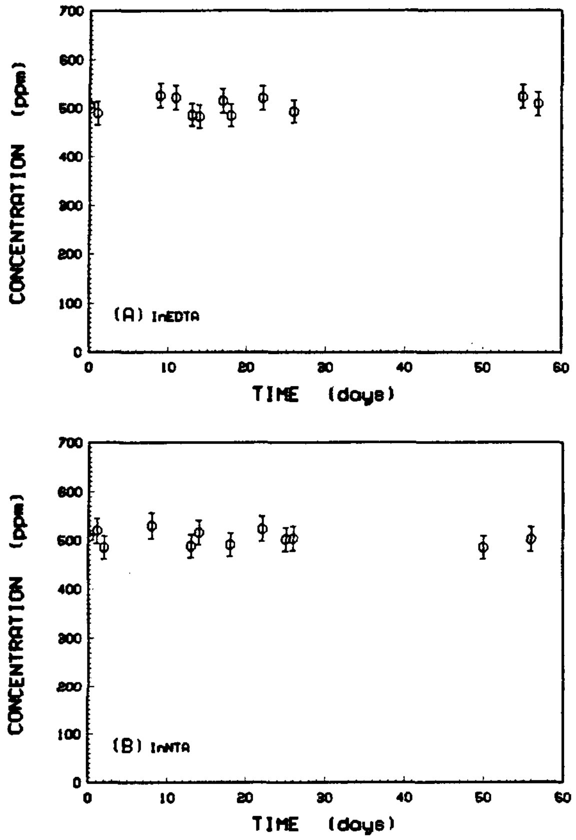

Figure 1. Indium chelated time stability behavior

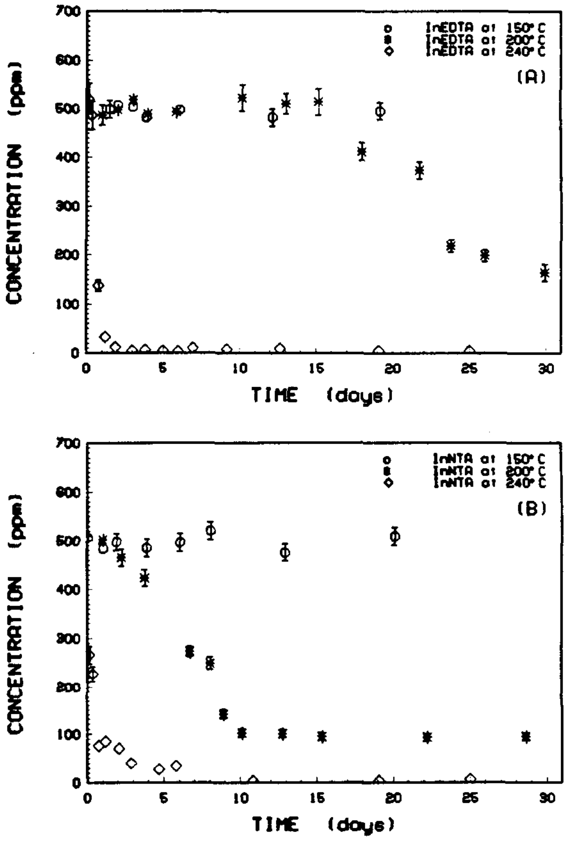

Figure 2. Indium chelated thermal stability behavior

tracer solution were transferred by pipette from each glass container to 15-ml polystyrene centrifuge tubes. After centrifugation at 3500 rpm for ten minutes, 2-ml of the supernatant liquid were removed from each centrifuge tube to a 6-ml Wheaton scintillation capsules for neutron irradiation and gamma-ray spectroscopy. Comparator standards were prepared and encapsulated with the unknown samples and were treated identically under the same irradiation flux conditions. The thermal stability high temperature experiments were conducted over 20 to 30 day periods. The pressure vessels were filled with 10-ml tracer solution and were sealed with teflon discs to prevent sample leakage. Geothermal reservoir temperatures were simulated with an air-bath. The vessels were taken from the air-bath and quickly quenched by immersion in a cool water-bath. The samples were transferred to centrifuge tubes and the detection of the soluble indium concentration was performed with the same analytical procedure as the one described for the room temperature experiments.

RESULTS AND DISCUSSION

The results of the tracer time stability investigations are given in parts A and B of Figure 1. The average concentration of 502 ppm indicates that there was no change in the soluble indium concentration during the experimental time. Any unchelated indium ions would be expected to adsorb onto container walls and to precipitate as indium hydroxide. The precision of the analytical procedure was estimated to be ±14 ppm. The error bars express only the counting error of the radioactivity measurements.

The experimental data from the high temperature runs are given in parts A and B of Figure 2. At 150°C, both chelated tracers were stable over the experimental period of 20 days. At 200°C, the soluble indium concentration of the InEDTA tracer solutions remained constant for 16 days, and then decreased with a measured rate constant of $k_{obs} \cong 0.09\ d^{-1}$. The time lag before the occurrence of any significant change in the total soluble indium concentration can be attributed to the secondary degradation products of EDTA. The thermal decomposition of InNTA at 200°C showed a first order reaction with a measured rate constant of $k_{obs} \cong 0.16\ d^{-1}$. At 240°C the data were not suitable for quantitative analysis because the time required for the first few pressure vessels to reach air-bath temperature was an appreciable fraction of each heating period. Nonetheless, both indium chelated tracers showed rapid decomposition with rate constants greater than $1.8\ d^{-1}$.

CONCLUSIONS

From the experimental results it was concluded that the organic ligands EDTA and NTA form stable time persistent complexes with indium at room temperature. The results from the thermal stability measurements showed that indium chelated tracers can be used effectively in geothermal reservoirs with temperatures up to about 200°C for transit times of at least 20 days. The data indicate that indium chelation with EDTA is favorable for high-temperature reservoirs.

Experiments are underway to investigate the effects of temperature and organic complexing ligands on the adsorption of indium on geothermal rock types, such as graywacke. Initial experiments are being run to determine adsorption and precipitation phenomena of In^{+3} at room and elevated temperatures.

ACKNOWLEDGEMENTS

The authors would like to thank Mike Thompson of USGS, Menlo Park for many stimulating discussions and for permission to the high-temperature laboratory; as well as Don Busick and Gary Warren of Health Physics, SLAC for allowing us to use the ^{252}Cf neutron source. This work was funded by U.S. Department of Energy under contract number DE-AT03-80SF11459.

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