Journal of the Korean Nuclear Society
Volume 6, Number 4, December 1974

≪Original≫ Laboratory Tests of Chromium-51 Complexes for Leak Detection in Pipes Carrying A Liquid Flow

You Sun Kim
Korea Atomic Energy Research Institute, Seoul, Korea

Byung Hyun Lee
Department of Nuclear Engineering, Han Yang University, Seoul, Korea

(Received Febuary 24, 1974)

Abstract

For detection and localization of leaks in closed vessels or pipes carrying liquid flow, ^{51}Cr-EDTA and ^{51}Cr-DTPA were synthesized and, the column and batch equilibrium experiments were carried out.

In the column experiment, the recovery of ^{51}Cr—EDTA is 100% in quartz sand and 80.9% in steel sawdust, and that of ^{51}Cr-DTPA is 77.4% in quartz sand and 6.4% in steel sawdust. The recovery curve. ^{51}Cr-DTPA system in steel sawdust does not show a certain plateau, exceptionally. In general, ^{51}Cr-EDTA is adsorbed less than ^{51}Cr-DTPA.

In the batch equilibrium experiment, the distribution coefficients(Kd) and effect of pH were investigated by using quartz sand, montmorillonite, steel sawdust, and mixed cement raw material as media. In general, the Kd values for ^{51}Cr-EDTA are lower than that of ^{51}Cr-DTPA. The Kd values for ^{51}Cr-EDTA are almost zero at pH 6.0, 7.0, and 8.0.

요 약

유동액체를 수송하는 도관 또는 폐용기의 누설의 탐지 및 위치한정을 위하여 ^{51}Cr-EDTA 및 ^{51}Cr-DTPA를 합성하고 Column Experiment 그리고 pH를 변화시켜 Batch equilibrium Experiment를 하였다. Column Experiment에서 ^{51}Cr-EDTA의 회수율은 Quartz sand에서 100%, Steel sawdust에서 80.9% 그리고 ^{51}Cr-DTPA는 Quartz sand에서 77.4%, Steel sawdust에서 6.4%이다.

Recovery curve는 Steel sawdust ^{51}Cr-DTPA system에서 예외로 일정한 plateau를 표시하지 않는다. Batch Equilibrium Experiment에서 분배계수 Kd와 pH와의 관계를 Quartz asand, Montmorillonite, steel sawdust 그리고 Mixed Cement Raw Material등을 매질로 하여 검토하였다. 일반적으로 ^{51}Cr-EDTA에 대한 Kd값이 ^{51}Cr-DTPA에 대한 그것보다 낮다. ^{51}Cr-EDTA에 대한 Kd값이 pH 6.0, 7.0, 그리고 8.0에서 거의 0이 된다.

1. Introduction

The application of radioactive isotopes as tracers in the study of a manufacturing process does not include any side reaction, and the measurement of tracer radiation can be made with an extreme sensitivity. Therefore, the greatest pratical industrial advntages have been shown from radioisotopes.

Radioactive tracing has been developed for detection and localization of leaks in closed vessels or pipes carrying liquid or gaseous flow[1,2]. Two principal requirements for such tracers are:

1) Low loss through contact with the vessels or pipes.

Tracers are lost from solution because of adsorption, ion exchange, diffusion, dilution, hydrolysis with resultant precipitation and filtration, and possibly other physical and chemical reactions.

2) Stability in the solution.

To test several probable substances against these standards, the laboratory tests have been made for stability and losses from solution when the tracers pass through the vessels or pipes. In general, anions and complexes are subject to less loss than cations. The tracer should be taken into account the production of radioisotopes, half-life, and radiation characteristic to suit the experimental conditions. The suitable tracers with medium half-life can be found among the metallic chelates. The chelate may be neutral or charged. Many chelating agents are known, and since there are several metals which have radioactive isotopes with half-lives in weeks or months, the number of possible chelate tracers are very large. The best known chelating agent is ethylenediamine-tetraacetic acid, EDTA. Examples of useful complexes are EDTA complexes of $^{114m}In(t_{\frac{1}{2}}=50d)$. ^{51}Cr $(t_{\frac{1}{2}}=27.8d)$, $^{46}Sc(t_{\frac{1}{2}}=84d)$ and $^{124}Sb(t_{\frac{1}{2}}=60d)$.

Table 1. Stability constants(log K) of metal EDTA and DTPA complexes.

Cation	EDTA	DTPA
Magnesium	8.69	9.02
Barium	7.76	8.63
Strontium	8.63	9.68
Manganese	13.47	15.11
Iron(Ⅰ)	14.22	16.66
Iron(Ⅱ)	25.10	28.60
Zinc	16.58	18.14
Nickel	18.45	20.21
Cobalt	16.10	19.00
Copper(Ⅱ)	18.38	21.03
Mercury	21.80	26.70

Table 2. Column experiment: Recovery of ^{51}Cr-EDTA and ^{51}Cr-DTPA in quartz sand and steel sawdust.

Medium \ Tracer	^{51}Cr-EDTA	^{51}Cr-DTPA
Quartz Sand	100%	77.4%
Steel Sawdust	80.9%	6.4%

Chromium-51 possesses several favourable properties; *i.e.* absence of beta-radiation, and the low energy of the gamma-radiation(0.323 Mev. ~8%). The soft gamma radiation permits good localization of the tracer. The stability constant of the ^{51}Cr-EDTA complex is of the order of 10^{24}. Diethylenetriaminepentaacetic acid, DTPA, forms more stable complex than EDTA. The stability constants(log K) of the more common EDTA and DTPA chelates are compared in the table 1.[3]

In this study, ^{51}Cr-EDTA and ^{51}Cr-DTPA were selected for the tracers, and column and batch equilibrium experiments varying pH were carried out, where the properties of the exchange complex (e.g. montmorillonite) and the stability constant of the complex may be

effected by pH change[4]. The following materials were chosen as the packing material for the colum and the medium for the bath equilibrium experiment, which are widely used in the manufacturing process:

a) Quartz sand (50-100 mesh): SiO_2, 96%; Al_2O_3, 2%; Fe_2O_3, 0.13%; Na_2O, 0.3%; K_2O, 0.13%.

b) Montmorillonite (50-100mesh): SiO_2, 49.32 %; Al_2O_3, 28.31%; Fe_2O_3, 77.5%; CaO, 0.96 %; Na_2O, 0.48%; K_2O, 0.28%; TiO_2, 0.38%.

c) Steel sawdust, coated with rust. (5-10mm×2mm×0.2mm)

d) Mixed cement raw matererial (100-200 mesh): Limestone: 86.70%; Clay, 5.16%; Shale, 3.43%; Sandstone, 4.08%; Iron ore, 0.63%.

2. Experimental

1) Preparation of Complexes

a) ^{51}Cr-EDTA

Neutron-irradiated chromium metal was dissolved in an excess of 6 M-HCl, and the solution was filtered. A solution of equivalent amount of disodium ethylenediaminetetraacetate was added to the solution, the pH was adjusted lower than 3, and the mixture solution was warmed on the water bath at 80-90°C for about one hour. At this stage the green solution yielded a violet colouration. After the solution was cooled, ^{51}Cr-EDTA was purified by passing through a Dowex-50 cation exchange resin column.

The chemical purity of ^{51}Cr-EDTA was determined by paper-electrophoresis method, and the radiochemical purity of ^{51}Cr-EDTA was determined by using multichannel gamma scintillation spectrophotometer.

b) ^{51}Cr-DTPA

^{51}Cr-DTPA was prepared by the procedure with similar to that of ^{51}Cr-EDTA, except DTPA was dissolved in the presence of 0.1 M-NaOH. The chemical purity and the radiochemical purity were determined by the procedure with similar to that of ^{51}Cr-EDTA.

Table 3. Batch equilibrium experiment: Kd values for ^{51}Cr-EDTA in quartz Sand, montmorillonite, steel sawdust and cement raw material.

Medium \ pH	2.5	6.0	7.0	8.0
Quartz Sand	0.101	0.000	0.009	0
Montmorillonite	0.136	0.012	0.020	0
Steel Sawdust	0.149	0.033	0.033	0
Cement Raw Material	0.056	0.035	0.053	0

2) Laboratory Tests

a) Column Experiment

Laboratory equipment (Fig. 1) consists of a column (500mm×50mm), automatic fraction collector, tracer solution and water supply, and a micro air-pump. The column was packed with quartz sand or steel sawdust; then water was pumped through it, followed by tracer solution (Carrier concentration of 10 p.p.m at a pH 6.0; that of the orainary water), and then water was again pumped through the column. The flow rate was adjusted 2.0-2.5ml/min. and the column operation was carried out at room temperature, 5ml of the sample was collected into a tube in the automatic fraction collector through a siphon, and was measured by an well-type gamma scintillation counter at 500V E.H.T.

b) Batch equilibrium experiment

In batch equilibrium experiment, 1 gm, of adsorbent, that is, quartz sand, montmorillonite steel sawdust and mixed cement raw material, and 10ml of tracer solution (^{51}Cr-

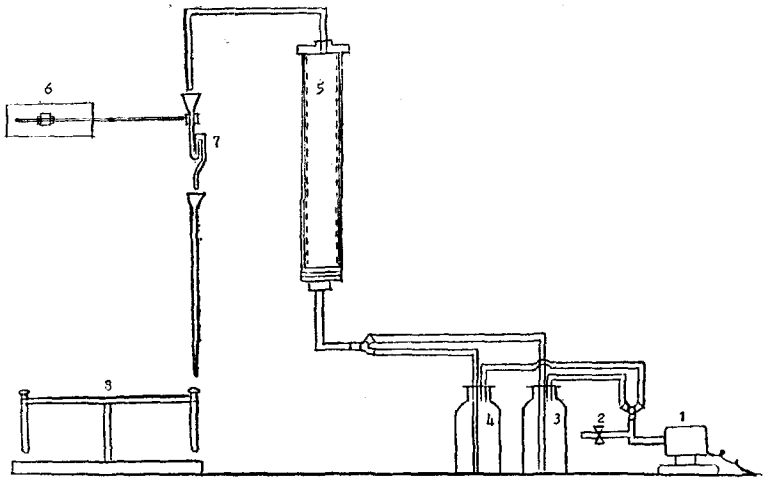

Fig. 1. Laboratory equipment for column tests.

1: Micro Air Pump
2: Pressure Relieve
3: Water Supply
4: Tracer Solution Supply
5: Column (500mm×50mm)
6: Volume Controller
7: Siphon
8: Automatic Fraction Collector

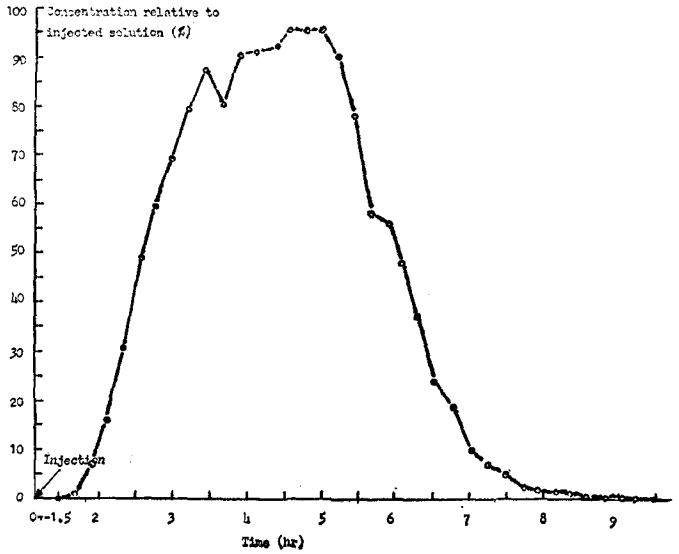

Fig. 2. Recovery curve for ^{51}Cr-EDTA in quartz sand.

EDTA, ^{51}Cr-DTPA) in low concentration (carrier concentration of 10 p.p.m.) were added into a 100-ml flask, and were shaken by using a wristaction (shaked for six hours at room temperature). The pH of tracer solutions was varied 2.5, 6.0, 7.0 and 8.0. Before and after mixing, the activities of supernatant solution were measured by an well-type gamma scintillation counter at 500V E.H.T.

3. Results

1) Laboratory Tests

a) Column Experiment

After the quartz sand or steel sawdust was packed into the column and ^{51}Cr-EDTA or

Table 4. Batch equilibooium experiment: Kd values for ^{51}Cr-DTPA in quartz sand, montmorillonite, steel sawdust, and cement raw material.

Medium \ pH	2.5	6.0	7.0	8.0
Quartz Sand	0.009	0.059	0.053	0.039
Montmorillonite	0.115	0.557	0.724	0.751
Steel Sawdust	0.458	0.214	0.099	0.087
Cement Raw Material	0.091	0.195	0.191	0.317

^{51}Cr-DTPA was passed through it, the recovery yields were expressed by the tracer activities as shown in Table 2, and the recovery curves were plotted by the concentration relative to injected solution versus time. Fig. 2 is a recovery curve for ^{51}Cr-EDTA against quartz sand; Fig. 3, ^{51}Cr-EDTA against steel sawdust; Fig. 4, ^{51}Cr-DTPA against quartz sand; and Fig. 5, ^{51}Cr-DTPA against steel sawdust.

b) Batch equilibrium experiment

For the batch equilibrium experiment, results were expressed as distribution coefficient(Kd) values, relating the specific adsorbed activity to the specific activity in the liquid phase. Kd value is calculated by the following equation:

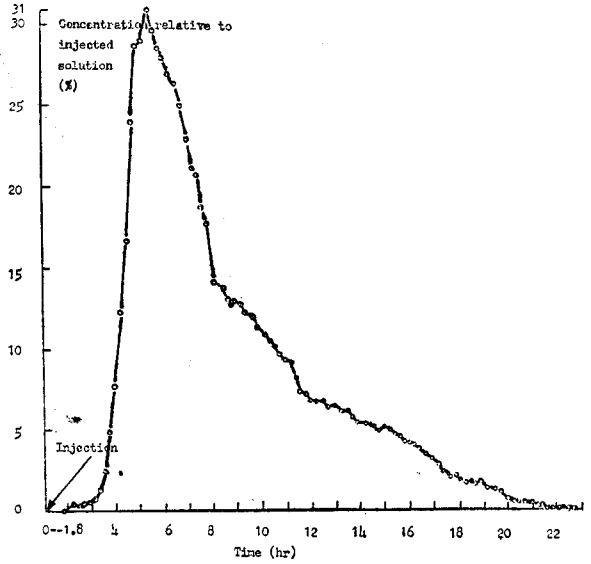

Fig. 3. Recovery curve for ^{51}Cr-EDTA in steel sawdust.

$$Kd = \frac{\text{Count-rate of adsorbent}}{\text{Count-rate of supernatant solution}} \times \frac{\text{ml. of the liquid phase}}{\text{gm. of adsorbent}}$$

Table 3 shows Kd values for ^{51}Cr-EDTA in quartz sand, montmorillonite, steel sawdust, and mixed cement raw material. Table 4 shows Kd values for ^{51}Cr-DTPA in quartz sand, montmorillonite, steel sawdust, and mixed cement raw material. The Kd value should be zero for an ideal tracer. The values

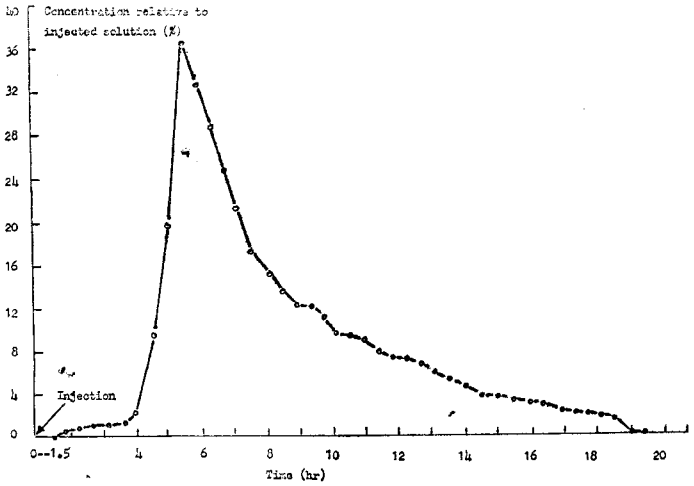

Fig. 4. Recovery curve for ^{51}Cr-DTPA in quartz sand.

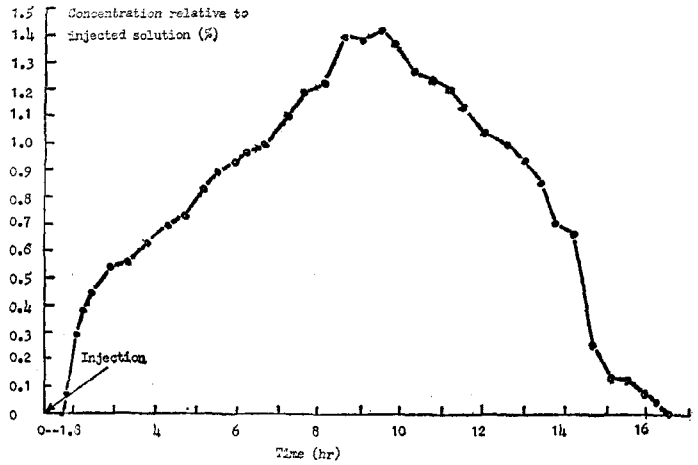

Fig. 5. Recovery curve for ^{51}Cr-DTPA in steel sawdust.

are dependent on the time of contact between adsorbent and tracer solution.

4. Discussion

In the column experiment, the break-through appeared one and a half hour in quartz sand, and one hour and fifty minutes in steel sawdust, after ^{51}-EDTA or ^{51}Cr-DTPA was injected. In quartz sand ^{51}-EDTA system, two hours later from the break-through a constant level concentration was reached, within the limits of the statistical error due to measurement. Finally, the curve sloped down a few hours after injection was stopped. The activity decreased exponentially towards zero. In steel sawdust ^{51}Cr-EDTA system, three hours later from the break-through, and in quartz sand in quartz sand ^{51}Cr-DTPA system, fours hours later, a peak was reached, respectively, In steel sawdust ^{51}Cr-DTPA system, seven hours later, maximum was reached without a certain peak and then curve sloped down.

^{51}Cr-EDTA is not adsorbed in quartz sand and its recovery yield is 100%, However, ^{51}Cr-EDTA is adsorbed in steel sawdust and its recovery yield is 80.9%. The recovery yields of ^{51}Cr-DTPA are 77.4% for quartz sand, and 6.4% for steel sawdust. The stability constants of metal chelates are generally known as DTPA complexes have higher values than EDTA complexes. But these appear reverse order in case of chromium chelates. The exchange reaction bet ween hydrated ferric oxide, the principal element of steel rust, and ^{51}Cr-DTPA is considered.

Kd values for ^{51}Cr-EDTA are low; it is relatively high at pH 2.5, and is almost zero at pH 6.0, 7.0 and 8.0. In ^{51}Cr-DTPA, the order is as follows: Order of Kd values at

Media	Order of Kd values at pH
Quartz sand	2.5<6.0~7.0>8.0
Montmorillonite	2.5<6.0<7.0<8.0
Steel sawdust	2.5>6.0>7.0>8.0
Cement raw material	2.5<6.0~7.0<8.0

The Kd value increases as the pH of the tracer solution decreases in steel sawdust. That is, the rate of ion exchange increases at the lower pH. In montmorillonite ^{51}Cr DTPA ststem and cement raw material ^{51}Cr-DTPA system, the rate of ion exchange increases at higher pH. In general, the Kd values for ^{51}Cr-EDTA are lower than that for ^{51}Cr-DTPA. It is assumed that the stability constant of ^{51}Cr-EDTA is higher than that of ^{51}Cr-DTPA as indicated in column experiment.

5. Conclusion

^{51}Cr-EDTA and Cr^{51}-DTPA were evaluated as to their suitability for detection and localization of leaks in closed vessels or pipes carrying liquid flow. From the result, it can be seen that ^{51}Cr-EDTA is more suitable tracer rather than ^{51}Cr-DTPA for detection and localization of leaks. ^{51}Cr-EDTA, which shows Kd values unrelated with the pH, is more useful in the solution of higher pH.

This investigation should be followed by laboratory tests as follows:

1) Time of contact.

Adsorption, exchange, and diffusion are affected by the time of contact between medium and tracer solution. If the velocity of liquid flow is known in a manufacturing process, the flow rate in the column experiment is to be controlled.

2) The nature of the liquid medium. particulary, the influence of salts may be expected in various fluids used in tae process.

Acknowledgement

The authors would like to express their appreciations for the laboratory works done by Mr. K. H. Hahn throughout this investigation.

References

1) INTERNATIONAL ATOMIC ENERGY AGENCY, Industrial Radioisotope Economics, Technical Report Series No. 40, IAEA(Vienna) 1965.

2) INTENATIONAL ATOMIC ENERGY AGENCY, peaceful Uses of Atomic Energy, Vol. 14, IAEA (Vienna) 1972.

3) J. BJERRUM, G. SCHWARZENBACH and L. G. SILLEN, "Stability Constants of Metal-Ion Complexes, with Solubility Products of Inorganic Substances. Part I. Organic Ligands. Part Ⅱ. Inorganic Ligands". Chemical Society, London, 1957, 1958.

4) D. CARROLL, Bull. Geol. Soc. Amer. **70**, 749 (1959)