d

THE SOLUBILITY OF KRYPTON IN HYDROFRACTURE GROUT AT ELEVATED PRESSURES*

C. L. Fitzgerald
J. C. Mailen

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

CONF-820303--46

DE83 015510

To be presented at the Waste Management '82 Conference
Tucson, Arizona, March 8-11, 1982

DISCLAIMER

THE SOLUBILITY OF KRYPTON IN HYDROFRACTURE GROUT AT ELEVATED PRESSURES

C. L. Fitzgerald
J. C. Mailen
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

INTRODUCTION

Nuclear fuel reprocessing facilities are expected to generate significant quantities of volatile radioactive wastes. The noble gas fission products (Kr, Xe) will be among these wastes, and U.S. Environmental Protection Agency regulations which will become effective in 1983 will limit the release of ^{85}Kr to ~15% of the amount present in the spent fuel assemblies.[1] Processes have been demonstrated to separate the noble gases from the main off-gas stream and reduce their volume to a manageable level.[2,3] However, an acceptable method for their permanent disposal has not been sufficiently developed.

The injection of intermediate-level wastes into deep shale formations by the hydrofracture process has been used routinely to dispose of the waste solutions generated at Oak Ridge National Laboratory (ORNL).[4] An extension of this process to include the noble gas fission products has been the subject of several studies.[5,6] A direct gas injection method was recommended; and toward this end, a laboratory program to measure the solubility of krypton in the grout mixture at simulated process conditions was initiated.

The solubilities of krypton in water, simulated waste solution, and simulated grout at about 25°C and to pressures of 150 atm have been determined. The results are reported here.

THE HYDROFRACTURE PROCESS

Development of the hydrofracture process at ORNL began in 1959. The facility designed for the experimental tests has been used since 1966 for the routine disposal of intermediate-level wastes. After careful consideration of the extensive modifications that would be required to ensure its continued use, the decision was made to install a new facility. Design and construction of the new facility are now essentially complete. An engineering study was made of the modifications and additions that would be necessary to this facility in order to inject noble gases and grout simultaneously. It was concluded that such alterations would be feasible.

Current operation of the hydrofracture process is based on 3×10^5 L (80,000 gal) of liquid waste per injection. The addition of the grout-forming solids yields a volume of about 4.5×10^5 L (120,000 gal). The injection well is prepared for operation by using an abrasive jet to form a radial slot at the desired elevation. The fracture is initiated by water pressure; the grout mixture is then pumped at the rate of about 946 L/min (250 gal/min). Hydraulic pressures necessary for fracture have varied between 136 and 340 atm. After the grout injection is completed, the pressure at the well-head decreases to about 68 atm during grout solidification. Over the next 30 days, it gradually decreases to the hydrostatic head pressure of about 34 atm.

The Barnwell Nuclear Fuel Plant was selected for reference purposes for ^{85}Kr production. Operation of this plant at full capacity for 1 year would yield a cumulative volume (0°C, 1 atm) of about 150 m^3 of krypton, 1500 m^3 of xenon, and 1.5×10^6 m^3 of air. Processing this gas stream with the fluorocarbon absorption process should yield an end product of krypton as a 50% mixture in either xenon or argon.[3] Based on the composition of this product stream, the annual production of krypton will be contained in about 300 m^3 of gas mixture (0°C, 1 atm).

A solubility of krypton high enough to contain 300 m^3 in about 3×10^5 L of aqueous waste at the hydrostatic well-head pressure of 34 atm should give a stable system (exclusive of water migration). Although direct solubility measurements are not available, an estimate was made that a pressure of ~57 atm would be required to dissolve the krypton-xenon mixture in the aqueous component. The measurements described in the following section were made to verify this estimate.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The usual method of measuring the solubility of a gas in liquid by equilibration in a pressure bomb (i.e., by direct measurement of solubility in the liquid) is not applicable for this study because of experimental conditions and the grout mixture. A technique was selected whereby a known volume of krypton is transferred to a stirred reaction vessel of known volume and the solubility is calculated from pressure differences. The hardware for this system consists of a krypton transfer vessel, a stirred autoclave, and pressure transducers that cover the appropriate pressure range. The transfer vessel was fabricated in-house, and the autoclave is a commercial laboratory model with a magnetically coupled agitation (source reference) to minimize the possibility of leaks. A Teflon plug was machined to occupy most of the void volume of the autoclave above the sample container to minimize gaseous volume and thus to achieve maximum sensitivity. Low-pressure solubility measurements (3.4 atm) were made with low-range pressure transducers; measurements above 3.4 atm were made with a transducer having a range of either 0-136 or 0-340 atm.

The pressure transducers were calibrated by the Instrumentation and Controls Division in a test facility maintained for this purpose. Voltage outputs were measured to the nearest 0.001 V (out of 2 to 7 V), and the linearity of each instrument was excellent. Typical correlation coefficients for a linear least-squares fit of the calibration data were greater than 0.999.

Accurate measurements of the volumes of the krypton transfer vessel and the autoclave are equally important. The volume of the transfer vessel was measured by filling it and the associated plumbing with water. This volume was then used to calculate the volume of the autoclave by measuring pressure changes in the two containers after transferring krypton. The volumes of the transfer vessel and autoclave (with liquid sample) were found to be 0.856 and 0.051 L, respectively.

The solubility of krypton in water at 1 atm was measured to check the accuracy of the system and technique. It was determined experimentally that an equilibration time of 3 h was required; this time, along with a 165-mL sample volume, was used for all experiments. The desired amount of krypton was admitted to the autoclave below the surface of the sample at about 20 mL/min (volume at operating pressure) while stirring at 40 rpm. The krypton solubility was calculated from differential-pressure measurements of both vessels at the end of the equilibration period.

The solubility of krypton in water at 25°C is reported to be 0.0515 cm^3 (NTP) per gram of water when the partial pressure of the gas is 1 atm.[7] We measured corresponding values of 0.0546 and 0.0524 at 24.8°C. A value of 0.0535 at 24.7°C is reported in Ref. 7; the average value we obtained at 24.8°C was also 0.0535. The good agreement of these values confirms the usefulness of our technique.

EXPERIMENTAL RESULTS

The solubility of krypton was measured in water, simulated intermediate-level waste, and hydrofracture grout. The composition of the simulated intermediate-level waste is shown in Table I. The density of the solution is 1.0783 g/mL at 25°C.

Table I. Composition of Simulated ILW

Compound	Concentration ($\underline{M}$)
NaOH	0.18
$Al(NO_3)_3$	0.007
NH_4NO_3	0.003
$NaNO_3$	0.81
NaCl	0.093
Na_2SO_4	0.094
Na_2CO_3	0.19

The solids in the grout mixture were 38.5% Portland cement, 38.5% fly ash, 15.3% attapulgite clay, 7.7% pottery clay, and a trace of sugar to extend the setting time. The grout was prepared by adding 719 g of this mixture to a liter of waste solution. This gave a slurry with an apparent density of 1.3825 g/mL.

The results of the measurement of krypton solubility in water, waste solution, and grout mixture are shown in Figs. 1, 2, and 3, respectively. The measurements for the grout mixture were made at pressures up to 150 atm. The measurements for water and the waste solution were discontinued at lower pressures (120 and 95 atm, respectively). The solubilities of krypton in water, waste solution, and grout mixture at 24.7°C and 1 atm were found to be 0.0535, 0.0277, and 0.0775 cm^3/mL (STP), respectively. The solubility in water obeys Henry's law up to 5 atm; solubilities in the waste solution and grout mixture obey Henry's law to 7.75 atm. At about 15 atm, the krypton solubility values in water, waste solution, and grout mixture were 1.43, 1.14, and 1.76 cm^3/mL (STP), respectively. The compressibility of krypton at pressures above 20 atm is significant.[8] The experimental data in Ref. 8 were fitted by a least-squares method to the equation

$$y = -0.000006X^2 + 0.003423X + 0.965303,$$

where X = the observed pressure (atm) and y = ideal pressure/ observed pressure. This correction was used in all calculations of solubility at pressures above 20 atm. The same technique was used to fit the experimental solubility data to empirical equations to aid in interpolation. The equations are:

for water, $s = 0.000183P^2 + 0.087463P - 0.101554$, (1)
for waste solution, $s = 0.000129P^2 + 0.080985P - 0.206041$, (2)
for grout mixture, $s = 0.000247P^2 + 0.108873P - 0.189720$, (3)

where P = observed pressure in atm and s = krypton solubility in cm^3(STP)/mL. These equations fit the data well at pressures above 10 atm; Henry's law is adequate below 10 atm. The reduced solubility in the waste solution relative to water is due to the salting out of the krypton. The positive deviations from Henry's law at elevated pressure increase the solubility of krypton under the conditions of grout storage; the reason for the deviation is not known. We were not able to find any references to krypton solubility at this temperature as a function of pressure. However, there is reference to a crystalline clathrate hydrate ($8Kr \cdot 46H_2O$) at 0°C and 14.5 atm that gives a solubility of 216 mL Kr (STP)/mL H_2O.[9] The increased solubility of krypton in the grout mixture is probably due to surface adsorption on one or several components in the mixture.

The contribution of the krypton solubility to the aqueous component of the grout mixture is also shown in Fig. 3. The difference in total solubility and the contribution of the aqueous component should behave according to existing relations for
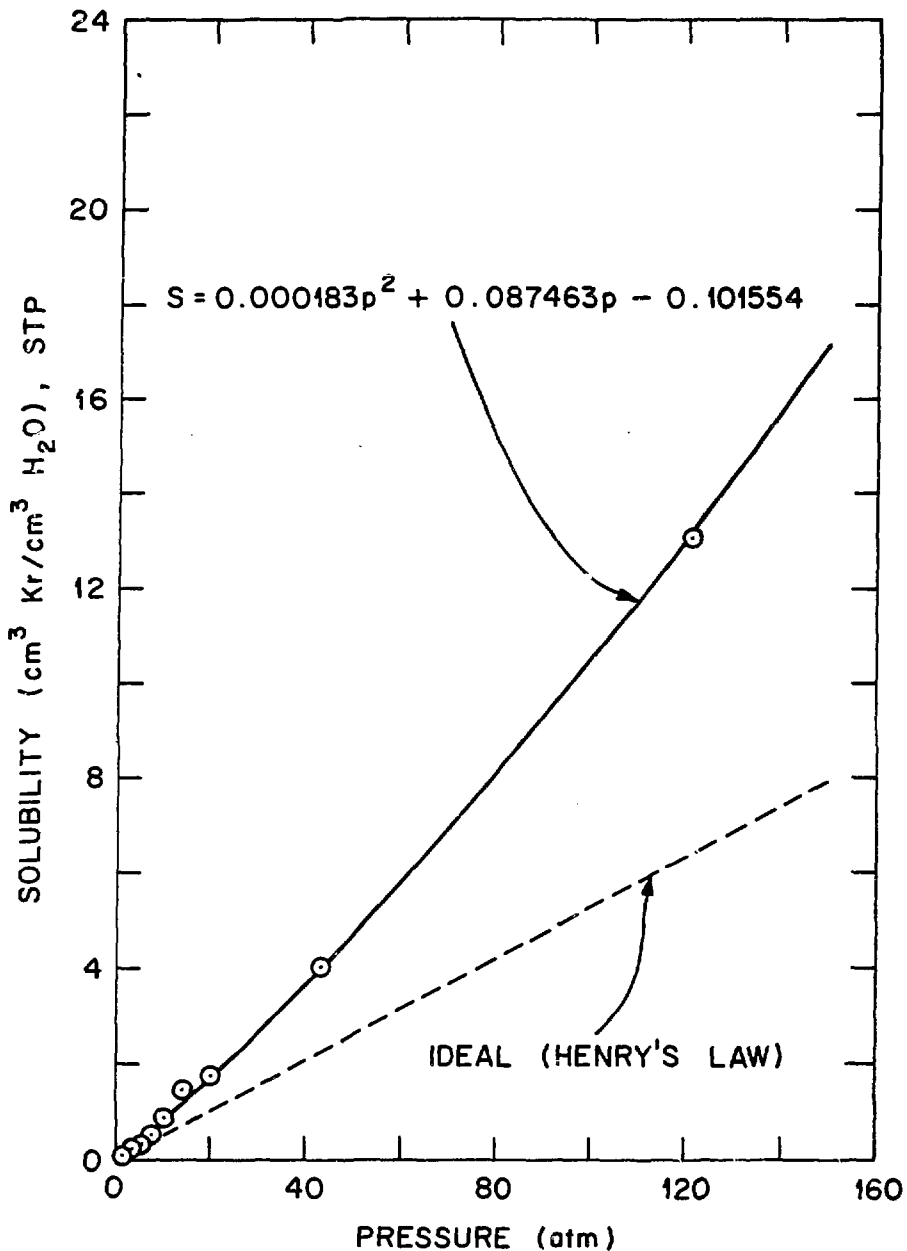
Figure 1. Solubility of Krypton in Water as a Function of Pressure.

SOLUBILITY (cm³ Kr/cm³ WASTE SOLUTION), STP

PRESSURE (atm)

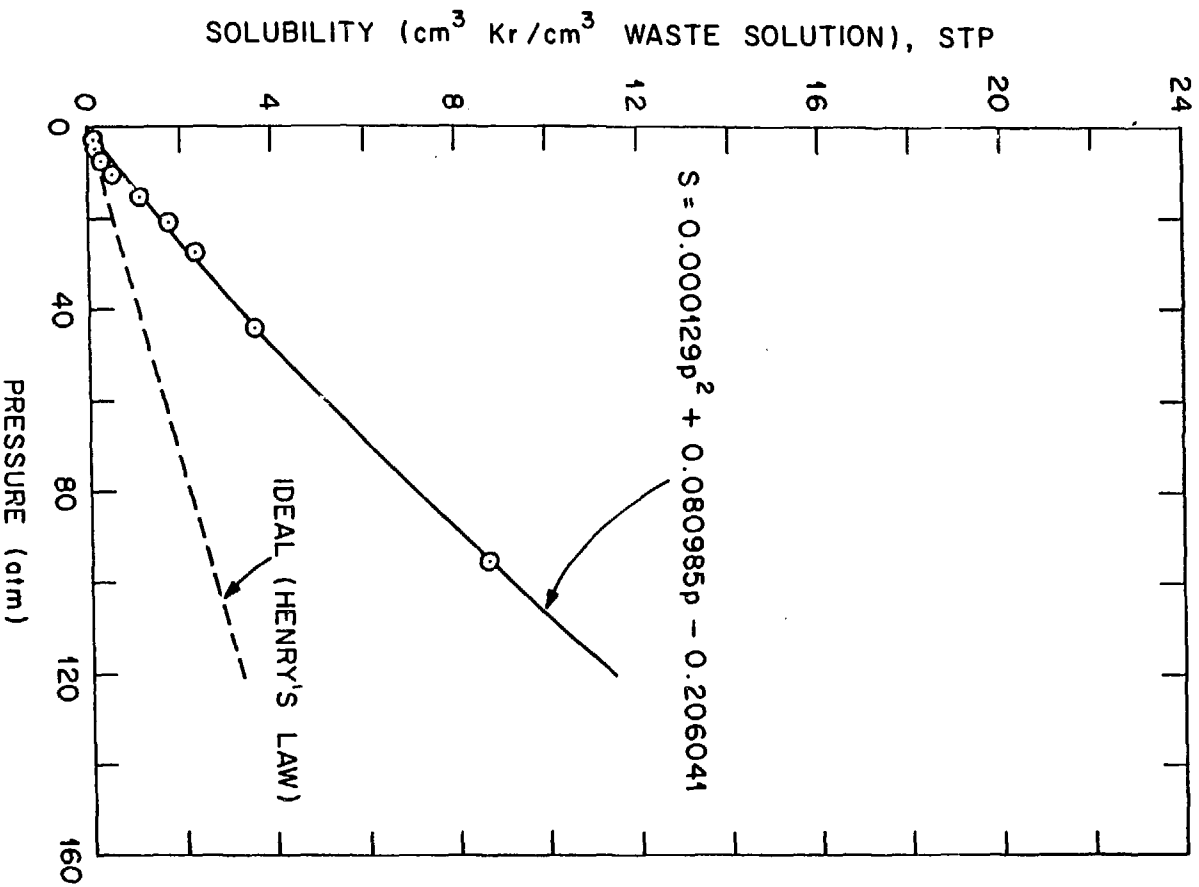$S = 0.000129p^2 + 0.080985p - 0.206041$

IDEAL (HENRY'S LAW)

ORNL DWG 82-7

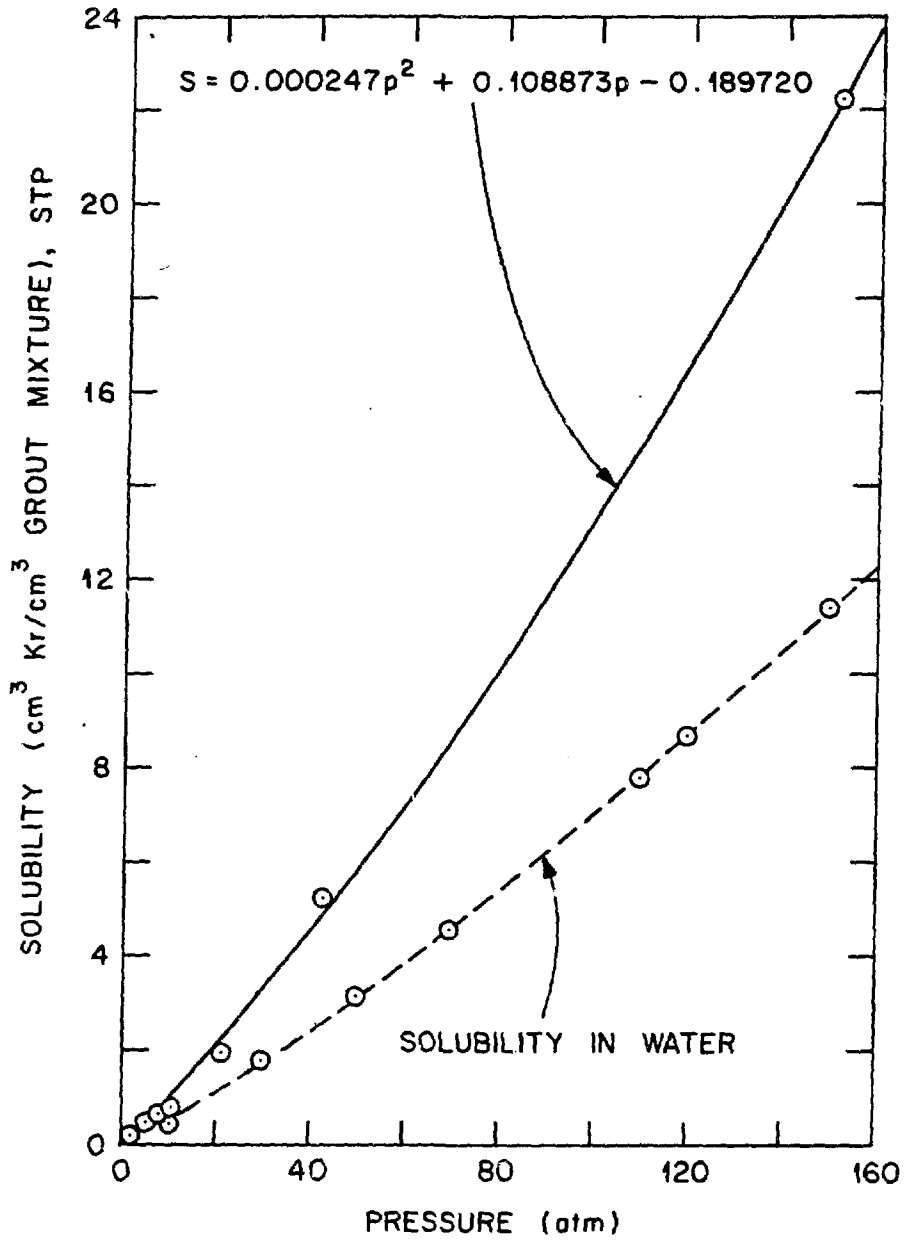Figure 2. Solubility of Krypton in Waste Solution as a Function of Pressure.

Figure 3. Solubility of Krypton in Grout Mixture as a Function of Pressure.

adsorption if this is the case. Since the adsorption is from a liquid to a solid surface and not a gas-solid interface, the data cover a narrow pressure range. The Freundlich relation, $s = ap^X$, generally fits experimental data fairly well over a limited pressure range. As shown in Fig. 4, the fit of the experimental data for excess solubility is quite good. The constants for the relation are indicated on the plot.

Interpolation of the experimental data shows that a krypton partial pressure of about 10 atm would be adequate to dissolve the krypton generated each year by the reference reprocessing plant in the annual hydrofracture grout injection at ORNL. The grout mixture is injected with a hydrostatic head up to 340 atm at the injection site. The grout itself consists of the aqueous waste solution, the solid components of the grout, and small air bubbles. The injected krypton and xenon would probably, for the most part, dissolve in the solution and adsorb on the solid particles of the grout. A small amount could exist in the gas bubbles at a partial pressure determined by the equilibrium between krypton dissolved in the grout mixture and gaseous krypton as measured in these studies, or about 10 atm. This partial pressure would be essentially independent of the hydrostatic head and would depend only on the ratio of krypton to grout as long as the air volume in the grout is small. The fraction of the krypton contained in the gas bubbles, of course, would depend on the volume of air contained in the grout mixture. At an underground static pressure of about 34 atm, and with a small air volume relative to the injected krypton, the krypton will constitute about 30% of the gas bubbles.

CONCLUSIONS

The results of these studies show that preliminary calculations of krypton solubility based on the aqueous component of the hydrofracture grout were overly pessimistic. The volume of noble gas generated annually by the reference reprocessing plant would be soluble in the annual hydrofracture grout injection at ORNL at about 10 atm. The amount of krypton in the gas phase would depend on the amount of air in the hydrofracture grout mixture. At 34 atm, and with a small air volume relative to the injected krypton, the krypton would constitute about 30% of the gas bubbles.

The disposal of krypton via injection with hydrofracture grout seems to be a viable process. The next logical steps would be to determine the krypton diffusion rate at injection conditions, and possibly to perform a test injection. At present, the schedule for future work is uncertain since funds for this project have been reduced significantly.
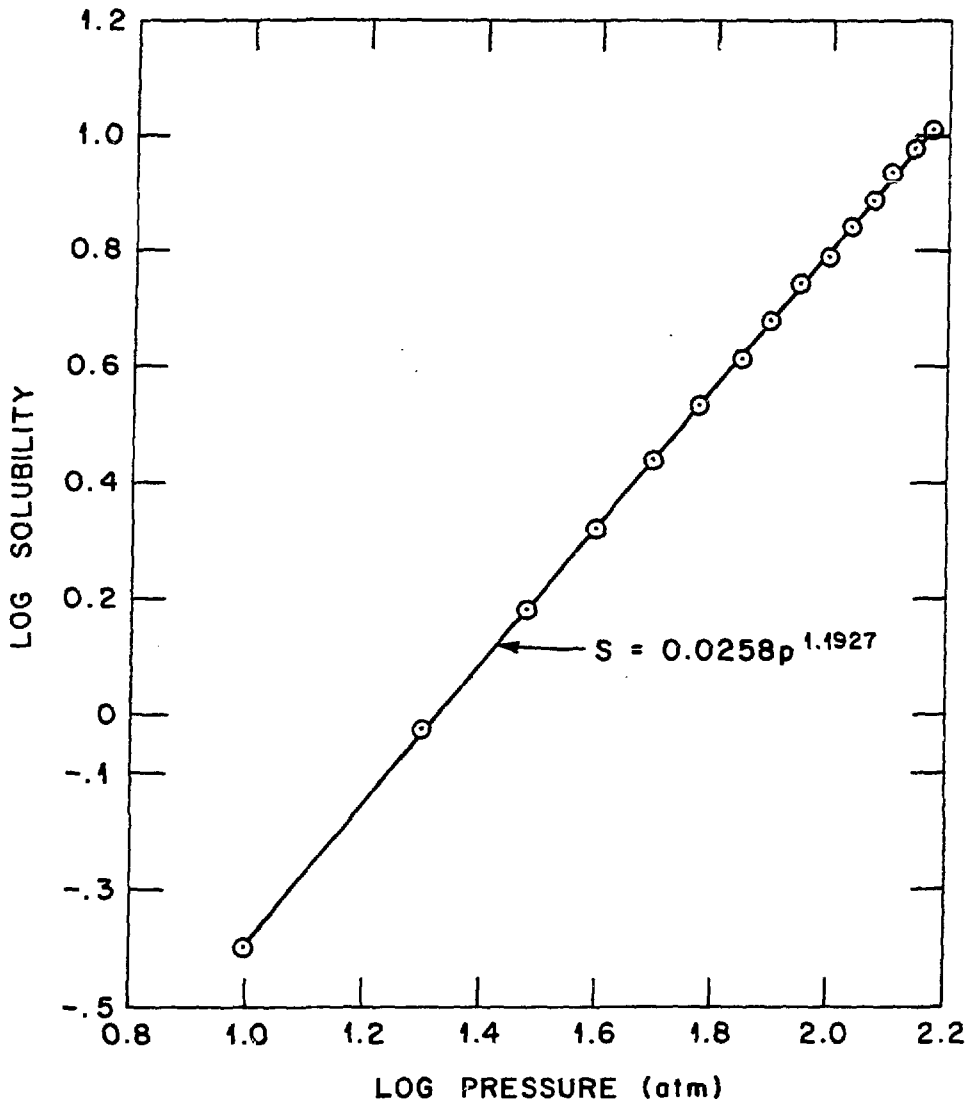
Figure 4. Freundlich Plot of Krypton Adsorption on Grout Mixture.

REFERENCES

1. United States Environmental Protection Agency (USEPA), Code of Federal Regulations, Title 40, Part 190.
2. M. J. Stephenson et al., "Experimental Demonstration of the Selective Adsorption Process for ^{85}Kr," pp. 293-98 in Proceedings of the 13th AEC Air Cleaning Conference, CONF-740807 (August 1974).
3. M. J. Stephenson and R. S. Eby, Development of the FASTER Process for Removing Krypton-85, Carbon-14, and Other Contaminants from the Off-Gas of Fuel Reprocessing Plants, K-GD-1398 (1976).
4. H. O. Weeren, An Evaluation of Waste Disposal by Shale Fracturing, ORNL/TM-5209 (February 1976).
5. J. H. Shaffer and J. O. Blomeke, Hydraulic Fracturing as a Method for the Disposal of Volatile Radioactive Wastes, ORNL/TM-6931 (August 1979).
6. F. J. Peretz, M. E. Muller, and P. Y. Pan, Krypton-85 Hydrofracture Engineering Feasibility and Safety Evaluation, ORNL/ENG/TM-22 (July 1981).
7. T. J. Morrison and N. B. Johnstone, J. Chem. Soc. 101(10), 3441 (1954).
8. James A. Beattie, James S. Brierley, and Roland J. Barriault, J. Chem. Phys. 20(10), 1613 (152).
9. J. H. Jeffrey and R. K. McMullen, Prog. Inorg. Chem. 8, 43 (1967).