Title	Irradiation experiments of simulated wastes of carbonate slurry
Author(s)	Nagaishi Ryuji, Motooka Takafumi, Yamagishi Isao
Citation	Proceedings of 2016 EFCOG Nuclear & Facility Safety Workshop, 6p.
Text Version	Published Journal Article
URL	https://jopss.jaea.go.jp/search/servlet/search?5056441
DOI	2023.3.17 現在なし
Right	© The Author(s) Published by Energy Facility Contractors Group.

Irradiation Experiments of Simulated Wastes of Carbonate Slurry

Ryuji Nagaishi
Takafumi Motooka
Isao Yamagishi
Japan Atomic Energy Agency (JAEA); nagaishi.ryuji@jaea.go.jp,
motoka.takafumi@jaea.go.jp, yamagishi.isao@jaea.go.jp

Introduction

Overflow of water from waste storage tanks of High Integrity Containers (HIC) in the multi-nuclide removal equipment (Advanced Liquid Processing System, ALPS) was discovered at Fukushima Daiichi Nuclear Power Station (NPS) in April 2015 [1], 5 months after decontaminated at a basic condition in ALPS. The mechanism causing the overflow, though not understood very well at the time, was considered to originate from “water radiolysis” by beta rays from Sr-90 and its daughter of Y-90 in high-viscous carbonate slurry as radioactive wastes in HIC. Energy of beta rays absorbed in the slurry can be estimated from the concentrations of nuclides: dose rate was 20-40 Gy/h and accumulated dose became close to 150 kGy in April 2015.

To elucidate that for chemical safety in the waste storage, irradiation experiments of simulated carbonate slurry by gamma ray have been conducted in CLADS, JAEA in cooperation with TEPCO, TOSHIBA and KURITA: in order of chemical evolution to the overflow, (1) measurements of radiolytic gas products from aqueous solutions contained in the slurry, (2) observations of volume change of the slurry during the irradiation, and (3) property analysis of the slurry before and after the irradiation.

Methods: Preparation and Irradiation of Slurry

The simulated carbonate slurry and its treated water were obtained from KURITA, who prepared them in similar way to co-precipitation treatment at pH = 12 with a cross flow filter in ALPS. Concentrations of chloride ion (Cl^-) and suspended solids (SS: $CaCO_3$ and $Mg(OH)_2$) in the slurry were 6,000 ppm and 95 g/L, respectively. Density and viscosity of the slurry at room temperature were 1.06 g/mL and 157 mPa•s, respectively. The treated water could easily dilute the slurry to prepare diluted ones. Dependences of viscosity and density on the SS concentration in the slurry were measured as shown in Figure 1 and 2, respectively.

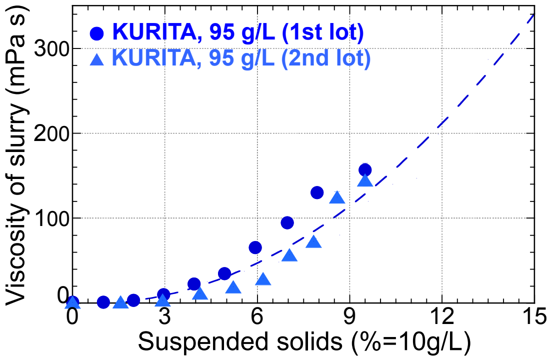

Figure 1 Dependence of viscosity of slurry on concentration of suspended solids.

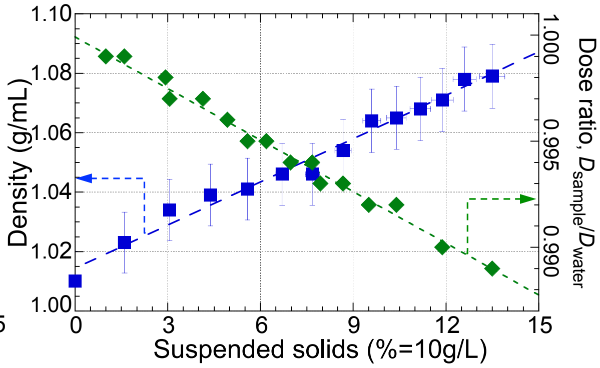

Figure 2 Dependence of density of slurry on concentration of suspended solids.

Both of the viscosity and density increased with increasing the SS concentration qualitatively, and the tendency of viscosity was dependent on the production lot of slurry in KURITA, indicating difficulty in reproducing the slurry.

The samples were irradiated at room temperature by gamma rays (average energy: 1.25 MeV) from Co-60 sources at Takasaki Advanced Radiation Research Institute, JAEA (National Institutes for Quantum and Radiological Science and Technology (QST) at present) [2]. It can be noted that according to Klein-Nishina formula for Compton scattering of photons, average energy of recoiled electrons from the gamma ray is about 55 % of the gamma-ray energy equal to 0.588 MeV, which is between average energies of beta rays from Sr-90 (0.196) and Y-90 (0.934) [3].

Dosimetry was made mainly with aqueous dichromate ($K_2Cr_2O_7$) solution and solid-state cellulose triacetate (CTA) film dosimeters [4]. Then absorbed dose of sample was estimated from those of the dosimeters, assuming that mass energy-absorption coefficient [5] is proportional to absorbed dose. Dose ratio of the slurry to water was estimated as a function of the SS concentration as shown in Fig. 2. The sample dose of slurry can be further separated into those of aqueous solution and SS at their "electron fractions" [Appendix A], and that of aqueous solution only results in water radiolysis to generate gas products in the slurry.

Results

(1) Measurements of gas products by water radiolysis in the slurry

In order to clarify kinds and amounts of radiolytic gas products, and to understand radiolysis behavior in the slurry, this first experiment has been made. Samples were the 95 g/L slurry and its diluted ones, and aqueous solutions of seawater and pure water for comparison. Each sample was filled in a glass vial (inner diameter: 14 mm) at a required volume, sealed with a cap, and irradiated by gamma rays at dose rate of 4-6 kGy/h up to accumulated dose within 25 kGy. After the irradiation, gas was sampled at a constant volume from the headspace of vial, and concentrations of hydrogen molecule (H_2) and carbon dioxide (CO_2) in the gas were individually measured by gas chromatography (GC). Concentrations of hydrogen peroxide (H_2O_2) and oxygen molecule (O_2) dissolved in the sample were measured by iodine coulometric titration and by spectrometric analysis with O_2 sensor, respectively.

The radiolytic gas products in the slurry could be considered to be H_2, O_2 and CO_2: H_2 is formed as one of the primary products, O_2 by thermal decomposition of the primary product of H_2O_2, and CO_2 from dimerization of secondary products of carbonate radical ($\bullet CO_3^-$) [6]. In the experiment, H_2 and O_2 (<10 % of the H_2 amount) were observed but not CO_2. No observation of CO_2 indicates its dissolution to aqueous solution ($CO_2 + H_2O = H_2CO_3$) in the slurry. It was confirmed by simple experiments of standard CO_2 gases contacting with aqueous solutions in sealed vials. Thus H_2 was found out to be the main gas product in the slurry.

The H_2 amount (mol/g) generated in the slurry increased linearly with increasing the sample dose (kGy=J/g), and a slope of the line passing at zero of the dose gave an observed yield (G-value, mol/J), $G(H_2)$, which was dependent on solutes present in aqueous solution contained in the slurry. It was predicted from "scavenging powers" for reactions of a radiolysis product of OH radical (•OH) with solutes [Appendix B] and then confirmed by the experiment that the H_2 generation was enhanced by solutes of not only halide ions (X^-: Cl, Br) as seawater components [7] but also carbonate ion (CO_3^{2-}) as an additive for the co-precipitation at pH = 12 [8].

The generation behavior can be further affected by the viscosity of slurry. Figure 3 shows dependence of the $G(H_2)$ on the SS concentration in the slurry. The viscosity is indicated in the upper axis. The yields were obtained from the H_2 measurement before (G_{stat}) and after (G_{total}) stirring the irradiated sample. The G_{total} was larger than the G_{stat}, and the G_{stat} decreased with increasing the viscosity while the G_{total} seemed to be almost constant within the SS concentration range in the experiment. The difference between the G_{total} and G_{stat} indicates the retention of H_2 in the slurry without stirred, where the phase of H_2 changed from dissolved species to bubbles.

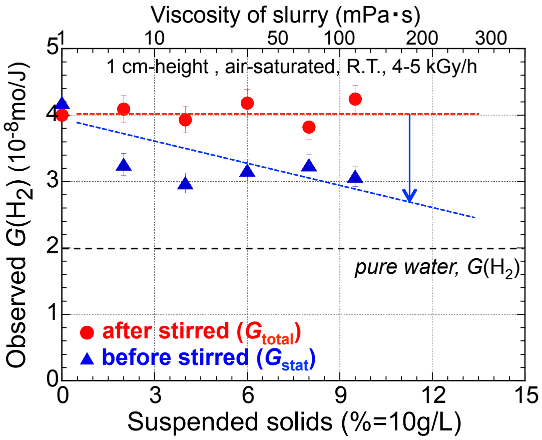

Figure 3 Dependence of observed yield of H_2 on concentration of suspended solids.

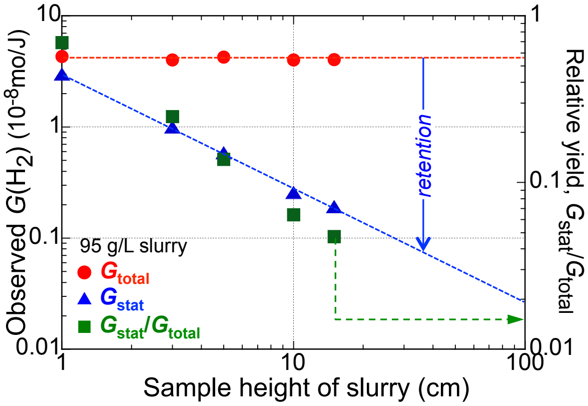

Figure 4 Dependence of observed yield of H_2 on sample height of slurry.

For the slurry with a constant viscosity, the yields were dependent on the sample height (10-200 mm) as shown in Figure 4. The G_{stat} decreased with increasing the height, and sequentially the relative yield of G_{stat}/G_{total}, indicating the H_2 emission fraction to the air, was estimated to become within 2 % at the height of 1,000 mm. These lead to the volume change of slurry by the irradiation at the higher dose.

(2) Observations of volume change of the slurry during the irradiation

In order to observe changes in volume and composition of the slurry followed by the retention of bubbles of the above gas products, and to compare them with the gas generation quantitatively, this second experiment has been made. A sample was the 95 g/L slurry. Each sample was filled in a quartz mess-cylinder (inner diameter: 20 mm) at a required volume (height), and irradiated in an open system at dose rate of 8.5 kGy/h up to accumulated dose within 500 kGy. At intervals scheduled during the periodic irradiation, levels of the slurry, and formations of bubbles in the slurry and of supernatant water above the slurry were measured and observed visually.

During the irradiation, increase of the level of slurry and irreversible formation of supernatant water above the slurry were observed as shown in Figure 5, where inhomogeneous spots of the bubbles could be also seen to be held in the slurry but not in the water naturally. On the other hand, in the slurry settled without irradiated for about 200 days, supernatant water was little formed within 2 % of the original height (100 mm) of slurry. These indicate that supernatant water was formed by the irradiation and/or the bubble formation rather than long-term settling without irradiated. Figure 6 shows the level increase as a function of the accumulated dose for 3 independent samples of the slurry. The level first increased up to 200 kGy, next attained to a maximum (about 10 mm) around 200 kGy, then decreased up to 300 kGy, and at the higher dose, these increase and decrease of level were repeated, where the maximum gradually decreased.

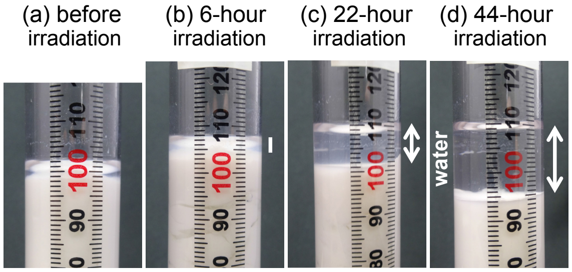

Figure 5 Changes of volume and composition of slurry during the irradiation (photos). The unit of measure was millimeter (mm).

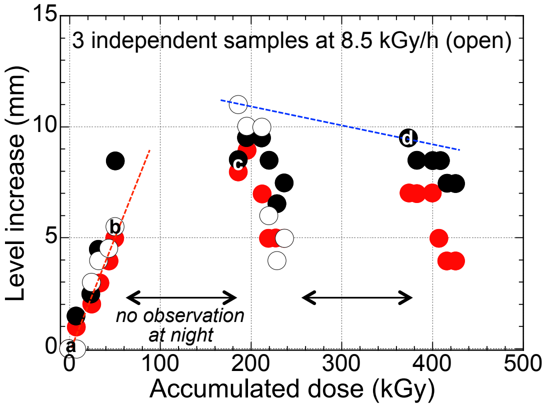

Figure 6 Variation of level increase of slurry with increasing accumulated dose.

The increase and decrease of level indicate retention (expansion of the slurry) and emission (shrinking) of the bubbles, respectively. The gradual decrease of maximum also suggests further formation of the supernatant water, meaning that amounts of water and the radiolytic gas products in the slurry decreased at the same time.

(3) Property analysis of the slurry before and after the irradiation

Long-term settling of the meter-sized slurry in an open system like HIC could bring about variations in its properties and composition in vertical direction, as well as the above changes by the irradiation. In order to understand them chemically, this third experiment has been made. The 95 g/L slurry without irradiated in an open system was applied as a sample to the settling test at first. Each sample was filled in the mess-cylinder in the same way to the above experiment (2).

After the test, the sample was divided into several parts in vertical direction, split slurry was sampled from each of the parts, and further filtrate water was obtained through ultrafiltration of the slurry. Then chemical analysis of the water was made: pH was measured by a pH meter, and concentrations of total carbonate ions (CO_3^{2-} and HCO_3^-) and element (Na, Mg, K, Ca, Sr, Cl) by a TOC (total organic carbon) analyzer and by ICP-OES (optical emission spectroscopy), respectively.

The pH and total carbonate concentration in the slurry settled with sealed by a film for 7 months were obtained at 4 division parts, and then illustrated in Figure 7, where the film allowed fair passing of the air between the inside and outside of mess-cylinder. Both of the values were quite different from those at the initial condition, indicating dissolution of CO_2 in the air to aqueous solution at the top of slurry regardless of the irradiation, as discussed in the above experiment (1). Since the diffusion of dissolved carbonate ion in the slurry is dependent on the viscosity and much slower than that in water, gradients of the carbonate concentration and subsequent pH would be formed in the vertical direction. Therefore, the carbonate concentration increased from the bottom to the top of slurry while the pH decreased in reverse. The pH decrease near the top of slurry further brought about dissolution of magnesium ions (mainly, Mg^{2+} and $MgOH^{+}$) from $Mg(OH)_2$ of the SS to aqueous solution in the slurry, as obviously shown in Figure 8.

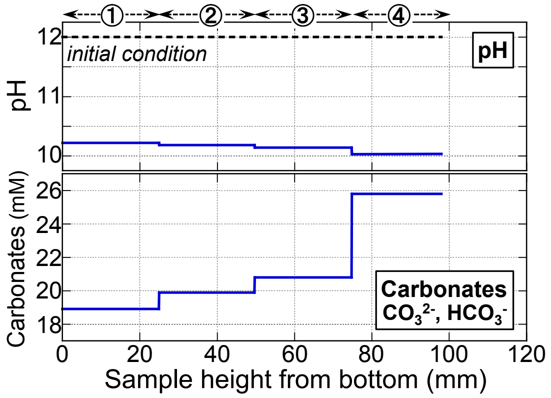

Figure 7 pH and total carbonate concentration in slurry after settled for 7 months. M=mol/L.

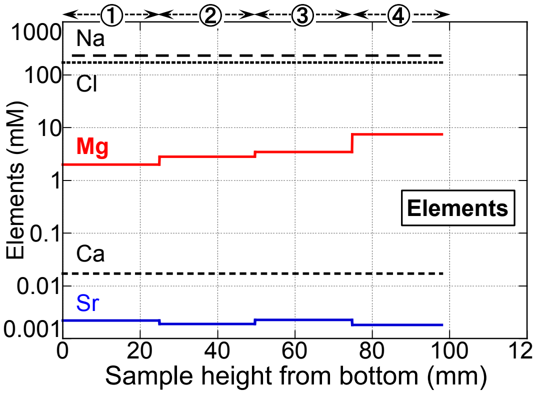

Figure 8 Dissolved element concentrations in slurry after settled for 7 months.

Conclusion

In the present experiments to elucidate the mechanism of overflow of water from HIC in ALPS at Fukushima Daiichi NPS, the reaction and retention behaviors of H_2 as main radiolytic gas product in the high-viscous fluid of slurry (1), the volume change of slurry and the formation of supernatant water by the high-dose irradiation (2), and variations in pH and composition in the vertical direction of slurry by the long-term settling (3) have been found out. These results in the experiments have been practically applied to quantitative estimation in the overflow of water, helpful for understanding of the mechanism. Further experiments are in progress.

References

1 TEPCO (Tokyo Electric Power Company), a press handout as one of Fukushima Daiichi NPS prompt reports (in Japanese), May 22, 2015. A file is available online <http://www.tepco.co.jp/nu/fukushimanp/handouts/2015/images/handouts_150522_07-j.pdf>.

2 I. Yamagishi, R. Nagaishi et al., "Characterization and storage of radioactive zeolite waste", J. Nucl. Sci. Technol., 51(7-8), 1044-1053 (2014).

3 R. Nagaishi, I. Yamagishi et al., "Revaluation of hydrogen generation by water radiolysis in SDS vessels at TMI-2 accident", Nuclear Plant Chemistry Conference 2014 (NPC 2014), #10224, Sapporo, Japan (2014). 9p paper is available online <http://jolissrch-inter.tokai-sc.jaea.go.jp/search/servlet/search?5048306>.

4 R. Tanaka, S. Mitsutomo et al., "Manual of CTA dose meter", JAERI-M 82-033, Japan Atomic Energy Research Institute (1982). In Japanese.

5 J. H. Hubbell, S. M. Seltzer, "Tables of X-ray mass attenuation coefficients and mass energy-absorption coefficients from 1 keV to 20 MeV for elements Z = 1 to 92 and 48 additional substances of dosimetric interest", NISTIR 5632, National Institute of Standards and Technology (1995).

6 Z. Cai, X. Li, Y. Katsumura, O. Urabe, "Radiolysis of bicarbonate and carbonate aqueous solutions: product analysis and simulation of radiolytic processes", Nucl. Technol., 136, 231-240 (2001).

7 R. Nagaishi, M. Inoue, R. Hino, T. Ogawa, "Consideration of radiolytic behavior in diluted and concentrated systems of seawater for computational simulation of hydrogen generation", Nuclear Plant Chemistry Conference 2014 (NPC 2014), #10242, Sapporo, Japan (2014).

8 G.V. Buxton, C.L. Greenstock et al., "Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals (•OH/•O⁻) in aqueous-solution", J. Phys. Chem. Ref. Data, 17(2), 513-886 (1988).

Appendices

A. Electron Fraction for Absorption of Radiation Energy

A fraction of radiation energy dissipated into a compound in matter is called an "electron fraction", originating from a fact that radiations of charged particles and photons interact with valence and/or orbital electrons inside atoms contained in matter. The fraction for the compound can be expressed by mass energy absorption coefficients, $(\mu/\rho)_{en}$, of the compound and matter (total) for photons [4].

$$f_i = \{w_i \, (\mu/\rho)_i\} \, / \sum \{w_i \, (\mu/\rho)_i\} \qquad \text{for compound, i} \qquad \text{(A.1)}$$

Where w_i denotes a weight fraction of the i compound. The sum of fractions for all compounds in matter ($\sum f_i$) is naturally unity. In the case of the simulated slurry containing 95 g/L SS, the electron fraction of SS was 8.2 % proportional to its concentration, in which those of precipitates of $CaCO_3$ and $Mg(OH)_2$ were 3.5 % and 4.7 %, respectively. Thus residual 91.8 % of energy of the gamma ray was dissipated into aqueous solution to generate gas products in the slurry in the experiments.

B. Scavenging Power for Reactions of Radical Products

When in a bimolecular reaction (A + B ->) concentration of one reactant (*e.g.*, A) is much higher than that of another reactant (B), *i.e.*, [A] » [B], the reaction becomes of pseudo first order, and then its rate constant, k_{1st} can be expressed as a product of second order rate constant, k_{2nd} for the original reaction and [A]. In the case of a reaction of a radical product, R with its scavenger, S ([S] » [R]) in radiation-induced reactions, the k_{1st} is called "scavenging power" especially in radiation chemistry.

$$k_{1st} = k_{2nd} \, [A] = k_{2nd} \, [S] \qquad \text{(A.2)}$$

The reciprocal of k_{1st} (s^{-1}) gives the lifetime (s) of pseudo first order reaction. In the case of seawater containing *ca*. 500 mmol/L (19,000 ppm) Cl^- and *ca*. 1 mmol/L (80 ppm) Br^-, their scavenging powers for •OH, k_{2nd} $[X^-]$ (s^{-1}) are 2.2×10^9 and 1.1×10^7, respectively [8]. Thus the lifetime of scavenging by Cl^- is 0.45 ns, leading to invasion of the scavenging reaction into inhomogeneous "spur reactions", which finish at 100 ns after water radiolysis in pure water. Scavenging power of 25 mmol/L CO_3^{2-} for •OH in the slurry, k_{2nd} $[CO_3^{2-}]$ becomes almost equal to that of Br^- in seawater.