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In Situ Composition Measurements of Bunsen Reaction Solution by Radiation Probes

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Abstract

Measuring equipments are integral to chemical process controls. A stable hydrogen production by the Iodine-Sulfur thermochemical water-splitting process is relatively difficult because of lack of existing in situ composition measurement techniques for multiple components and corrosive solution. Composition regulations of Bunsen reaction solution is particularly important, since a closed cycle system provided with this process causes that the many streams with different composition return to this section. Accordingly Bunsen solution becomes changeable composition. Radiation probes have a potential for applications to determine this multiple component solution while the non-contact approach avoids the corrosive issues. Moreover the probes have features of the promptness, contact-less and sequential use. Laboratory scale experiments to evaluate these possibilities of the measurement were conducted with use of simulated Bunsen solution, HIx solution and H₂SO₄ solution, containing HI, I₂, H₂SO₄ and H₂O and sealed radiation sources. Radiations were counted, which were interacted with the solutions in various compositions around room temperature contained in vessels. For HIx solution, the obtained counting rates were correlated with hydrogen volume concentrations; moreover, the application of the Monte Carlo method suggests possibilities that the detector responses for HIx solution by the radiation probes are predictable. For H₂SO₄ solution, iodine atoms had significant influences on the relationship between output values of two gamma-ray density meters, cesium source as higher energy and barium source as lower energy. This results suggest that the neutron-ray probe, the gamma-ray probes of both lower energy and higher energy have possibilities to determine the composition of Bunsen solution of HIx and H₂SO₄ solutions.

1 Introduction

Measurement equipments are indispensable to chemical process controls. A stable hydrogen production by the iodine-sulfur thermochemical water-splitting process (IS process) is relatively difficult because of lack of existing in situ composition measurement techniques for multiple components and corrosive solution. Figure 1 shows a brief reaction scheme for IS process; Bunsen reaction produces two types of corrosive and multicomponent acids around 100 °C, a HI rich solution (HIx solution) and a H₂SO₄ rich solution (H₂SO₄ solution), which are separated by two-phase separation phenomenon. The HI rich solution is purified and concentrated, then decomposed. Products of I₂ should be recycled to Bunsen section. The H₂SO₄ rich solution is also processed in this manner. Looking at the return streams, closed cycle system causes that the streams concentrate on Bunsen section. Many streams with different composition return, so that Bunsen solution becomes changeable composition; accordingly, solution compositions which are consequent on Bunsen reaction, such as the HI and H₂SO₄ rich solutions, become also changeable.

Compositions of the Hlx solution—this solution consists of, HI, I₂, H₂O, little amount of H₂SO₄—and the H₂SO₄ solution—this solution consists of, H₂SO₄, H₂O, little amount of HI and I₂—are important indices for stable process control, since throughputs of the Hlx solution and the H₂SO₄ solution should be adjusted with the assistance of these composition values depending on the targeted hydrogen production rate. Methods by radiation probes [1] have a potential for applications to determine this multiple component solution while the non-contact approach avoids the corrosive issues. Moreover these probes have features of the promptness, contact-less, and continuous use. The purpose of this study is to evaluate applicability of the methods for measuring the composition of the Hlx solution and the H₂SO₄ solution; we examined data which were obtained by a neutron moisture-meter and gamma-ray density- meters through laboratory-scale experiments with use of both simulated solutions.

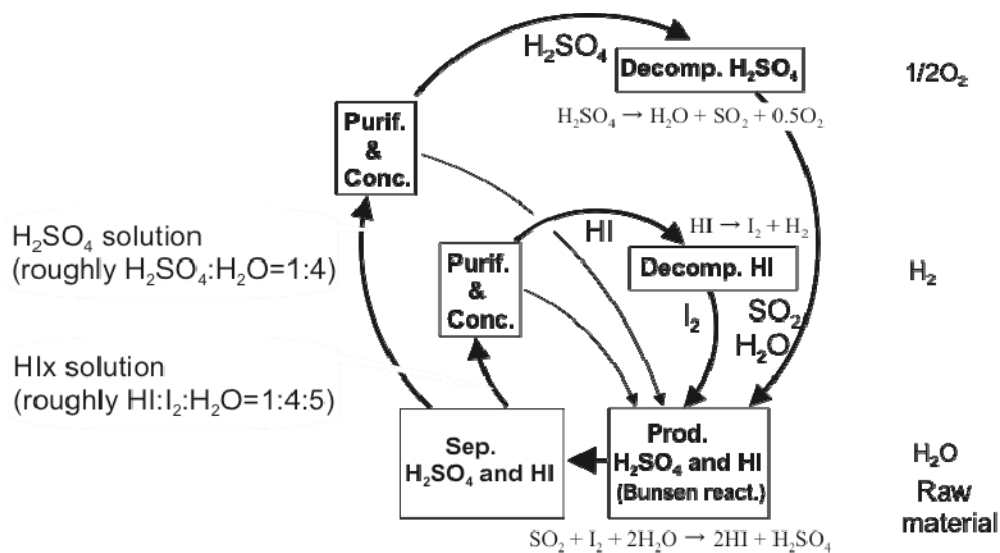


Figure 1: Reaction scheme of IS process. Solutions come out of Bunsen reaction are corrosive and multicomponent. Flow rate of Hlx solution and H₂SO₄ solution must be adjusted with assistance of composition of both solutions, which must be obtained by measurement methods, for stable plant operation.

2 In Situ Composition Measurement by Radiation Probes

Figure 2 shows a concept scheme of an in situ composition measurement by radiation probes which are gamma probes and a neutron probe. Two different gamma-ray sources in energy levels are employed to measure transmittance through a solution and a fast-neutron source emitting fast neutrons is employed to measure thermal neutrons moderated by interactions with hydrogen atoms. Integrations of data from three different probes have possibilities that compositions of four component, at a maximum, solutions are determined. Two or three probes can be used properly depending on a type of a solution.

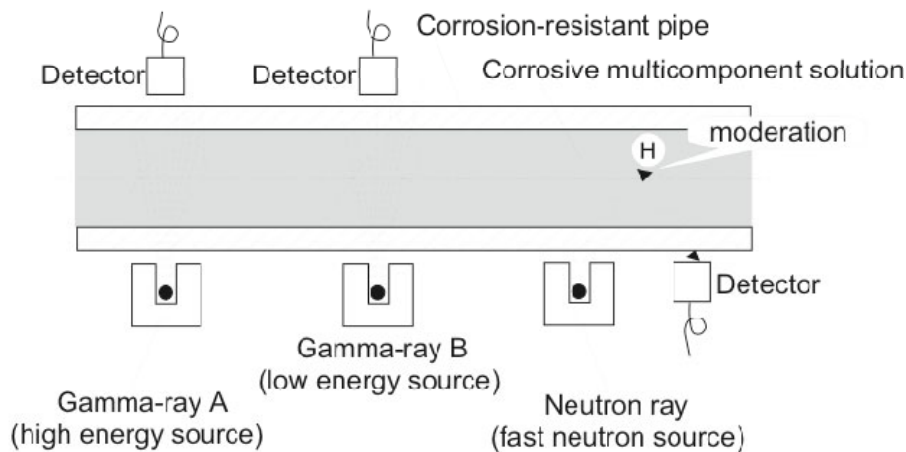


Figure 2: Conceptual scheme of in situ method in actual use to determine composition of corrosive and multicomponent solution. Non-contact approach avoids the corrosive issues. Two or three probes can be used properly depending on a type of a solution.

For the four-components solution of the HIx solution, the contained H_2SO_4 is minor component. To determine the composition of HIx solution requires the two radiation probes, since the solution is believed to be considered that this consists of three components of HI, I_2 , and H_2O . It has been generally recognized that the correspondences between the gamma-ray transmittance and solution densities are strong; moreover, there is a direct correlation between the densities of HIx solution and the iodine concentrations [2]. Accordingly, we focused on the hydrogen in HIx solution to explore residual or alternative information to complete the composition determination technique by the radiation probes. A system of neutron moisture meter employing the neutron ray provides advantages in quantification of the hydrogen.

For the four-components solution of the H_2SO_4 solution, the contained HI and I_2 are minor components; however, the heavy atom of the iodine, which has relatively high atomic number, affects a bulk density of this solution. Moreover the iodine atoms in both HI and I_2 supposedly have comparable effects. To determine the composition of H_2SO_4 solution requires the two radiation probes, since the solution is believed to be considered that this consists of three components of H_2SO_4 , H_2O , and the iodine. Accordingly, we chose two gamma-ray probes which are available with a cesium source and a barium source. A gamma-ray energy of the cesium source is higher than that of the barium source; a mass attenuation coefficient with the cesium source is nearly-constant with respect to object atoms ranging in broad atomic numbers, while a mass attenuation coefficient with the barium source is tending upward in accordance with a rise of the atomic numbers. The gamma-ray probe which has the higher energy determines the bulk density of the solution, besides the gamma-ray probe which has the lower energy probably determines the heaviest atom such as the iodine contained in the solution. A system of gamma-ray density meter employing the gamma-rays provides advantages in quantification of the bulk density and the heaviest atom concentration.

3 Experimental

A schematic of experimental apparatuses for HIx solution is shown in Figure 3. A container, which is open to the atmosphere, made of a plastic with diameter of 0.22 m was placed on a top board made of a stainless steel. A sensor assembly of a neutron moisture meter (NMA-2001, SHINKO EN&M) was put on to the underside of the top board; a fast-neutron source (californium, 2.5 MeV) and helium-3 proportional counters were built into this assembly, which were sealed by polyethylene walls. The thermal neutrons moderated by the interactions with the hydrogen atoms were counted by the counters housed in the assembly. Densities and compositions of the test solutions were determined by a oscillating density meter and a chemical titrator. Temperature of the solutions were obtained by a thermocouple. The test solutions were prepared by mixing regents of iodine powder and hydriodic acid. It is possible to take test solution in and out of the container by a tube pump. Levels of the solution in the container were calculated with weight changes of the tank, the densities of the test solutions, and the diameter of the container.

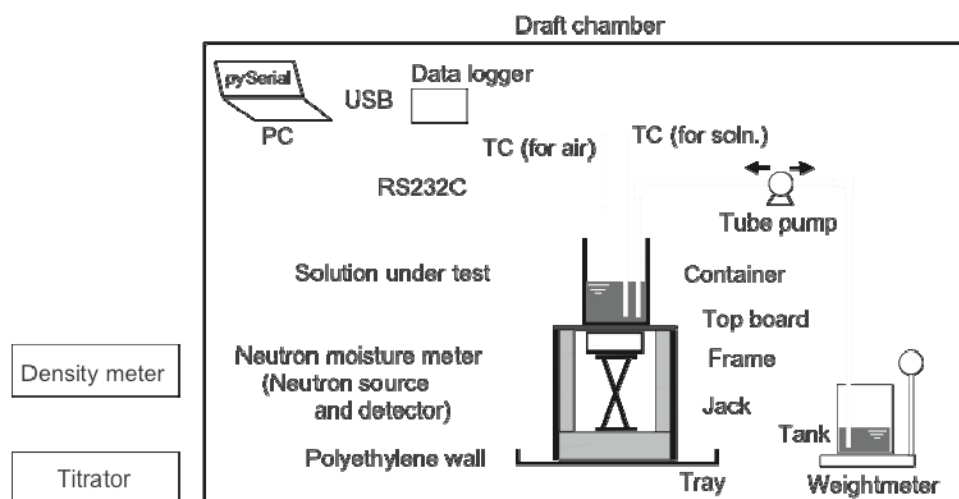


Figure 3: Experimental apparatus employing neutron moisture meter using fast neutron source to examine test solutions in container. Thermal neutrons moderated by interactions with hydrogen atoms were counted by detector. Densities and compositions of test solutions were determined by oscillating density meter and chemical titrator.

A schematic of experimental apparatuses for H_2SO_4 solution is shown in Figure 4. Graduated cylinders, which is open to the atmosphere, made of a glass with a inner diameter of 41.4 mm was placed on jacks. Two gamma-ray density meters (GD-4000, EARTHIX) were placed for each cylinder; either of gamma-ray source (cesium, 0.6 MeV; barium, 0.3 MeV) and a scintillation detector made up the density meter. Intensities of the gamma-rays which passes through substances and decay by the interactions with atoms were counted by the detector at opposite side of the source. The tests were carried out at room temperature. In advance of the tests, the meters were calibrated using two solutions (water, 1.0 g/cm^3 ; sulfuric acid 98 wt%, 1.83 g/cm^3) of known densities. A integral time of 300 seconds to

measure was set through trial examinations. The test solutions were prepared by mixing reagents of sulfuric acid, water, hydriodic acid, and iodine powder. Compositions of the test solutions were determined by weights of the reagents of known concentration in preparation procedure. Sulfur formations could occur in the preparation, so that such solutions were withdrawn from test solution.

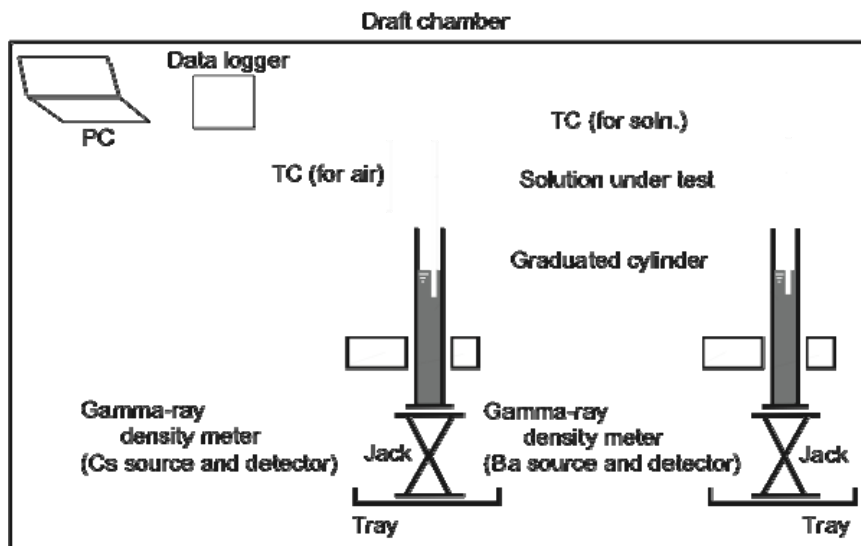


Figure 4: Experimental apparatus employing gamma-ray density meters using high-energy gamma-ray source and low-energy gamma-ray source to examine test solutions in graduated cylinders. Intensities of gamma-rays which passes through substances and decay by the interactions with atoms were counted by scintillation detector at opposite side of source.

4 Results and Discussion

For the HIx solution test, thought prior tests using water ($23.5\text{ }^{\circ}\text{C}$, $\rho=0.997\text{ g/cm}^3$) to examine solution levels on the counting rates, the counting rate at that the solution level equivalent to zero displays a significant value, since the apparatus materials itself affect the measured values. An effect on the counting rates against the solution level disappears as certain value of the solution level is exceeded. Accordingly, influences on the counting rates by difference of the solutions might be compared through the use of a difference between two values which are the counting rate at solution level of zero and that in the flat region. A result for a HI solution (without iodine) and two HIx solutions appears in Figure 5. The volume concentration of hydrogen atom were calculated from measured densities and titrated composition. This figure illustrates the counting rates are correlated with the volume concentration; this fact suggests that the neutron probe has a possibility to determine the composition of HIx solution.

In order to develop a prediction method which enable to compute the counting rates for the measuring system, a Monte Carlo method was applied to this composition measuring system. For preliminary computation, a difference of the detector response between water and HIx solution was obtained, which suggests possibilities that the detector responses for HIx solution by the radiation probes are predictable.

For the H_2SO_4 solution test, sulfuric acids ($\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system) with various concentrations, sulfuric acid containing the hydriodic acid, and sulfuric acid containing the hydriodic acid and the iodine (below 1 mole%) were examined by two gamma-ray density meters. Figure 6 shows relationships between output values by the two density meters. Looking at the sulfuric acids which are free from the iodine atom, the densities with the cesium ray are proportionate to that of the barium ray. In cases of that the sulfuric acids contained HI or both HI and I_2 , the iodine atoms had significant influences on the relationship. The densities as output values obtained by using the barium gamma-ray, which has relatively low energy, showed higher values than true values because the mass attenuation coefficient with the barium source is high regarding to the iodine which has large atomic number. Plots, which were affected by the iodine, of each sulfuric acid concentration, $C_{\text{H}_2\text{SO}_4} = x_{\text{H}_2\text{SO}_4} / (x_{\text{H}_2\text{SO}_4} + x_{\text{H}_2\text{O}})$, were in lines, moreover the lines of each $C_{\text{H}_2\text{SO}_4}$ and the lines of the solutions containing no iodine crossed at the intersections which shows the concentrations as $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system. This result suggests that the gamma-ray probes of both lower energy and higher energy have a possibility to determine the composition of H_2SO_4 solution.

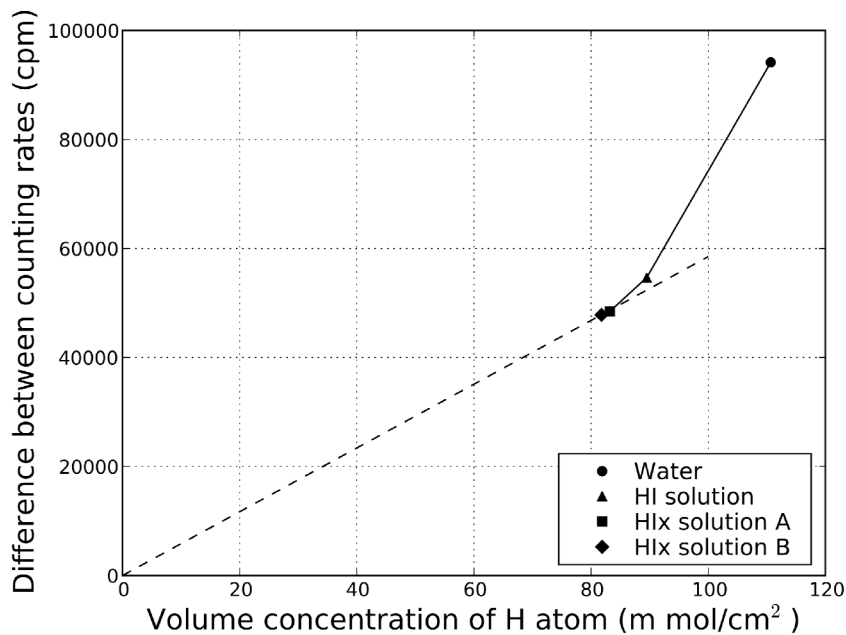


Figure 5: Counting rates of HI solution and Hlx solution by neutron moisture meter (HI solution, 23.5 °C, $\rho=1.691 \text{ g/cm}^3$, $x_{\text{HI}}:x_{\text{I}_2}:x_{\text{H}_2\text{O}}=0.154:0:0.846$; Hlx solution A, 22.5 °C, $\rho=1.861 \text{ g/cm}^3$, $x_{\text{HI}}:x_{\text{I}_2}:x_{\text{H}_2\text{O}}=0.146:0.026:0.828$; Hlx solution B, 21.5 °C, $\rho=1.881 \text{ g/cm}^3$, $x_{\text{HI}}:x_{\text{I}_2}:x_{\text{H}_2\text{O}}=0.090:0.057:0.853$). Values on vertical axis represent differences between counting rate at solution level of zero and that in region of sufficient solution levels.

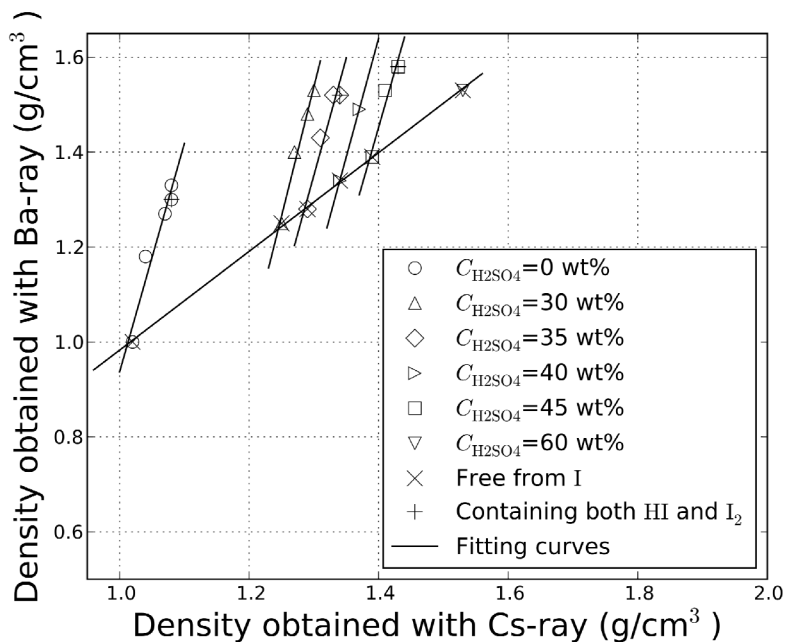


Figure 6: Relationships between output values by two gamma-ray density meters. Sulfuric acids without iodine atom, sulfuric acid containing hydriodic acid (below 1mole%), and sulfuric acid containing both hydriodic acid and iodine (below 1 mole%) were examined. $C_{H_2SO_4} = x_{H_2SO_4} / (x_{H_2SO_4} + x_{H_2O})$ means concentration as H₂SO₄-H₂O system.

5 Summary

The Measurement equipments are indispensable to chemical process controls. A stable hydrogen production by the Iodine-Sulfur thermochemical water-splitting process is relatively difficult because of the lack of existing in situ composition measurement techniques for multiple components and corrosive solution. Methods by radiation probes have a potential to determine the composition of this multiple component solution while the non-contact approach avoids the corrosive issues. We focused on the neutron-ray for HIx solution to explore the technique to determine the composition for HIx solution. As for H₂SO₄ solution, we chose two gamma-ray which are available with the cesium source (higher energy) and the barium source (lower energy). Laboratory-scale experiments to examine its applicability were conducted with use of both simulated solutions by the neutron moisture meter with the sealed radiation source and by the gamma-ray density meters with the sealed radiations sources. For HIx solution, the obtained counting rates were correlated with hydrogen volume concentrations; this fact suggests that the neutron ray is a candidate probe to determine the composition of HIx solution. Moreover, the application of the Monte Carlo method suggests possibilities that the detector responses for HIx solution by the radiation probes are predictable. Also, for H₂SO₄ solution, densities as output values with the cesium ray of the sulfuric acids, which are free from the iodine atom, were proportionate to that of the barium ray. In cases of that the sulfuric acids contained HI or both HI and I₂, the iodine atoms had significant influences on the relationship. This result suggests that the gamma-ray probes of

both lower energy and higher energy have a possibility to determine the composition of H₂SO₄ solution.

Acknowledgement

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