Abstract. The electrochemical reaction of water decomposition on a tiny platinum electrode was applied to detecting the cavern boundary of zero velocity. Measurements of cavern sizes and shape were carried out in a transparent carboxy vinyl polymer (CVP) solution and a CaCO₃ suspension. From the space distributions of time averaged current and its fluctuation, the cavern boundary of zero velocity was easily detected in both yield stress fluids. In CVP solution, the sizes of cavern of zero velocity were larger than those of the cavern visualized with dye.

Keywords: Cavern, yield stress, electrochemical reaction, non-Newtonian fluid, particle suspension.

1. INTRODUCTION

One of the critical problems in mixing yield stress fluids is that fluid motion ceases if the shear stress acting on the fluid is less than the yield stress. If the mixing power is insufficient, fluid motion is limited to a region around the rotating impeller while the fluid in the outer region stays stagnant. The inner limited flow region is called cavern.

In the previous studies on cavern, several techniques have been employed: visualization with dye [1,2], X-ray photographs [3], planar laser induced fluorescence [4,5] or ultraviolet fluorescence [4], flow observation with tracers [6], detection of flow with a hot film anemometer [7], an electroconductivity probe [8] or a thermocouple [9], electrical resistance tomography [10] and velocity measurements with LDA [11,12,13] or PIV [3]. Simple models have been proposed to relate cavern sizes with operational variables and rheological properties [6,7,13]. Recently CFD analyses were carried out to compare the calculated results with the cavern size and shape visualized by the fluorescence method [3,4] and with the velocity distributions measured with PIV [3]. Most of the investigations described above were conducted for homogeneous yield stress fluids such as carboxy vinyl polymer (CVP or Carbopol) and Xanthan gum solutions. Little is known about the cavern formed in particle suspensions with yield stress. The main reason for the lack of cavern investigation on particle suspensions may be attributed to the difficulties in applying the techniques adopted in homogeneous yield stress fluids to opaque particle suspensions.

We have developed a new technique of flow detection using the electrochemical reaction of water decomposition, which can be used in yield stress aqueous solutions including suspensions [14,15]. This paper describes a brief introduction to this technique, showing the main results obtained in the experiments carried out in a CVP solution and a CaCO₃ suspension with yield stress.
2. ELECTROCHEMICAL METHOD FOR FLOW DETECTION

2.1 Test fluids

The test fluids were a CVP solution of 0.1% in mass concentration and a CaCO₃ suspension of 59% in particle mass concentration. The CVP solution was prepared by adding NaOH to increase the viscosity. The CaCO₃ suspension was prepared by mixing CaCO₃ fine powder of 2.2 μm average diameter in water. Their flow curves measured with a cone-plate viscometer were well expressed by the Herschel-Bulkley model \( \tau = \tau_y + K\gamma^n \).

The electrochemical reaction controlled by mass transfer can be utilized for measuring liquid velocity [16]. In the ordinary measurement, electrolytes such as CuSO₄, KI or a mixture of K₄Fe(CN)₆ and K₃Fe(CN)₆ are used as the species for electrochemical reaction. However the addition of such substances to CVP solution caused a large decrease in viscosity and yield stress. Therefore the electrochemical reaction in this study was conducted without adding any species to the raw aqueous solution of CVP or suspension of CaCO₃.

2.2 Electrode and Test Equipment

Figure 1 shows the structure of the electrode used in this study. A fine platinum wire of 0.31mm diameter was inserted into a capillary glass tube, which was fused to expose the wire tip in 1mm length as the cathode and fixed in a stainless steel tube with an adhesive bond.

Figure 2 shows the test equipment. The electrode attached to a rotating arm was circulated in the test fluid contained in a stainless steel vessel of 300mm in diameter. DC voltage was applied between the platinum cathode and the anode of the stainless steel vessel through a slip junction and a resistance. The exposed area of the cathode is so small compared with that of the anode that the current is considered to be fully governed by the electrochemical reaction on the cathode. The current was measured from the voltage drop through the resistance.

2.3 Current Characteristics

Figure 3 shows variations of the current with the applied voltage when the probe was circulated at the velocity of 0.071 ms⁻¹. The current in the CVP solution increased exponentially and tiny bubbles were generated when the applied voltage exceeded 1V. This indicates that the current is caused by the cathodic decomposition of water. In the CaCO₃ suspension a plateau-like behavior appeared in the region from 0.5V to 0.7V, which suggests a possibility of electrochemical reduction of Ca²⁺ ion. The exponential increase at higher voltages is due to the decomposition of water.

Figure 4 shows dependencies of the current on probe velocity at the applied voltage of 1.0V. In both solutions the current increases only to a slight degree with probe velocity except for the region near zero velocity. An appreciable difference in current between zero and non-zero velocities reveals that the electrode can be used as a flow detector.
3. MEASUREMENT OF CAVERN SIZES AND SHAPE IN YIELD STRESS FLUIDS

3.1 Measurement in Carboxi Vinyl Polymer Solution

Figure 5 shows the experimental apparatus used for the CVP solution. An unbaffled cylindrical vessel of transparent acrylic resin was used as the mixing tank, which was installed in a transparent rectangular tank. The tank diameter was \( T = 290 \text{ mm} \). A Rushton turbine with six blades of diameter \( D = T/2 = 145 \text{ mm} \) was centrally mounted at a height of \( C = T/3 \) from the bottom. The Pt electrode shown in Figure 1 was attached to a traverser placed on a fixed plate. The Rushton turbine and the shaft made of stainless steel were used as anode. DC voltage was applied between the anode and cathode through a slip ring and a resistance for measuring the current. The impeller torque was measured by a strain gauge torque meter placed between the driving motor and the impeller shaft. The Reynolds number was calculated using the apparent viscosity based on the Metzner and Otto concept or \( \gamma \) with \( K_s = 11.6 \) for the Rushton turbine [17].

A radial distribution of time averaged current at \( z = 0 \) is shown in Figure 6, where the origin of the \( r \) and \( z \) coordinates is placed at the impeller center. The rotational speed is \( N = 1.0 \text{ s}^{-1} \) (\( Re = 14.9 \)). The electrode was traversed from the outer stagnant region toward the impeller region. Time fluctuations of the current are also shown at \( r = 88.5, 107.5 \) and \( 117.5 \text{ mm} \). The current did not fluctuate and kept a constant value in the stagnant region as shown on the record at \( r = 117.5 \text{ mm} \), but it increased and fluctuated with further decreasing \( r \).

![Figure 5 Experimental apparatus used for the measurement in CVP solution](image1)

![Figure 6 Radial distribution of time averaged current and fluctuation (EC denotes Electro-chemical reaction)](image2)
From the radial variations of the time averaged current and its fluctuation, the boundary of zero velocity was determined to be located at \( r = 113.5 \text{ mm} \).

Cavern visualization was also carried out under the same condition by injecting a tracer liquid colored with Congo Red into the impeller hub, from which the radius of the colored cavern was determined to be \( D_c/2 = 103.5 \text{ mm} \). The difference between the two cavern radiiues reveals that the fluid outside the visualized cavern boundary is not stagnant, as reported by Jaworski et al [6].

The time fluctuation at \( r = 88.5 \text{ mm} \) was composed of short and long period fluctuations. The short period was equal to one-sixth of the rotation period of impeller, which corresponds to the rotation period of blade since the impeller had six blades. The long period was 1.7 times the rotational period of impeller, which was also observed on the record measured at \( r = 107.5 \text{ mm} \). In the observation of the cavern colored with dye, the cavern boundary repeated a cyclic small expansion and contraction. The long period of the current fluctuation recorded on these charts coincided with the period of the cyclic expansion and contraction of cavern.

Figure 7 shows a comparison of the visualized cavern with the cavern boundary or contour of zero velocity determined with the electrochemical method. The boundary of the flow around the rotating shaft was also detected. The sizes of the cavern of zero velocity were larger than those of the visualized cavern. The upper and lower half heights of the cavern of zero velocity were defined as the \( z \) positions at the edge of the impeller disk or \( r = (1/2)(3/4)D = 54.4 \text{ mm} \).

The cavern diameters and half heights measured with both methods have been plotted in Figure 8. They hardly changed at \( Re < 10 \) but increased with increasing \( Re \) from 10. The cavern reached the vessel sidewall and the vessel bottom around the same Reynolds number. At the Reynolds number around \( 2 \times 10^2 \), the upper interface of the cavern reached the liquid surface and the whole liquid was agitated. The sizes of the visualized cavern were smaller than those of the cavern of zero velocity at every impeller speed.

### 3.2 Cavern Measurement in CaCO\(_3\) Suspension

The measurement of CaCO\(_3\) suspensions was carried out in a stainless steel vessel with \( T = 300 \text{ mm} \) by using a Rushton turbine, whose diameter \( D \) was equal to \( T/4 = 75 \text{ mm} \). The use of a smaller impeller was due to the limitation of the measuring limit of the torque meter used. The impeller and the shaft of stainless steel were used as anode.
Figure 9 shows radial variations of time averaged current and fluctuations at $N = 6.0 \text{ s}^{-1}$. At $r = 57.6 \text{mm}$ the current increased just after the probe had been traversed to this position and then decreased to a constant value without fluctuation. Hence the suspension was stagnant in the outer region of $r > 55.6 \text{ mm}$.

At $r = 54.6 \text{ mm}$ just inside the stagnant region the current fluctuated with time at first. Then the fluctuation ceased and the current settled down to the value measured in the stagnant region. This may be due to a blocking effect of the electrode against the flow or to an increase of particle concentration due to sedimentation. The latter may cause an increase in the yield stress that makes the flow stagnant. At $r = 50.6 \text{ mm}$ the current fluctuated intensively without showing the decreases in time observed at $r = 54.6$ and $55.6 \text{ mm}$. In the fluctuations at $r = 50.6 \text{mm}$ it was impossible to detect the frequency of blade passing or the cyclic behavior of expansion and contraction that had been observed in CVP measurement. The intensive fluctuation is likely caused by particle collision with the electrode. In the CaCO$_3$ measurements the cavern boundary of zero velocity could be easily determined from the sharp rise of time averaged current together with the variations of current fluctuation.

Figure 10 shows the cavern boundary of zero velocity determined at $N = 6.0 \text{ s}^{-1}$. The cavern shape is similar to that formed in CVP solution and the upper half height $H_u$ is nearly equal to the lower half height $H_l$. In addition, the boundary of the flow near the rotating shaft was also detected. Variations of the cavern diameter and its upper half height measured at the impeller disk tip are plotted against Reynolds number in Figure 11, which shows that the cavern grows keeping a geometrically similar shape with $H_u/D_c = 1/4$ or $H_l/D_c = 1/2$.

4. SUMMARY

From the current measurements of the electrochemical decomposition of water using a tiny platinum electrode in the carboxi vinyl polymer solution and the CaCO$_3$ suspension, it
has been confirmed that the electrode can be used as a detector of flow in aqueous yield stress solutions including particle suspensions. In the aqueous solution of carboxi vinyl polymer, which was used as Carbopol in many of the previous studies, it has been found that the fluid velocity is not zero on the boundary of the cavern visualized by injecting dye into the impeller hub.

5. REFERENCES