Adhesion Force Arising from Solid Salt Bridge Formed after Drying of Liquid Bridge

Yoshiyuki Endo, Yasuo Kousaka and Hidenori Onitsuka
Dept. of Chern. Eng., Univ. of Osaka Pref., *

Abstract

Water bridges formed among particles in industrial process often contain soluble impurities such as salts. When such bridges are exposed to dry air, water in the bridges vaporizes and the salts crystallize to form solid bridges.

Solid bridges between two glass spheres were formed from NaCl, KCl, KNO₃ and Na₂SO₄ solution by controlling the humidity, and their tensile strength was measured. It was found from these experiments that 1) the adhesion force of a solid salt bridge which was uniformly formed in the gap between two spheres was one to two orders of magnitude larger than that of a water bridge without crystallization; 2) the average adhesion force of solid bridges was proportional to the 1/2 power of the product of salt volume and particle radius; and 3) the adhesion force of bridges of NaCl and KCl was influenced by the surrounding humidity, which it was below their deliquescent points, because they adsorbed water until complete recrystallization took place.

1. Introduction

In most previous studies on such solid bridges, the strength in a consolidated state of a powder bed consisting of deliquescent particles as NaCl was studied1· 5· 7· 8, 10-12), and the adhesion force of a solid salt bridge formed by vaporizing water from a liquid bridge containing a small amount of soluble salts has never been studied.

2. Theoretical discussion

In this paper, two spheres of identical size as shown in Figure 1 are considered as particles. A liquid bridge containing the soluble salts is formed by the Kelvin effect and the effects of dissolving substances therein (effects of the vapor pressure drop on the surface of the liquid bridge, and as a result increase the size of the bridge)2l. Generally, in the case of particles used in industrial processes, the effect of the solutes is greater than the Kelvin effect, which is negligible3l, and the size and profile of a liquid bridge are determined by the relative humidity of the atmosphere, the kind and the amounts of solutes in the liquid bridge etc9). The adhesion force $F_L$ arising from a liquid bridge formed in such manner can be obtained from the following equation4):

$$ F_L = \pi p_L r_2^2 + 2\pi \sigma r_2 $$

where $r_2$ is the neck radius of the liquid bridge shown in Figure 1, and $p_L$ is the pressure deficiency in

* 1-1 Gakuen-cho, Sakai-shi 593 JAPAN
† This report was originally printed in Kagaku Kougaku Ronbunshu, 20, 542 (1994) in Japanese, before being translated into English with the permission of the editorial committee of the Soc. Chemical Engineers, Japan.
the liquid bridge, which depends on the size and profile of the bridge determined in the above manner. Thus, the liquid bridge adhesion force \( F_L \) is determined by the type and amount of solutes, the surrounding humidity, the size of the particles, the distance between the particles and the like. When a large liquid bridge is formed because of a large amount of solutes contained in the liquid bridge, or when the gap between the particles forming the bridge can be considered as \( h = 0 \), for a liquid bridge formed between two spheres of identical size, Eq. (1) can be approximated by the following equation:

\[
F_L = 2\pi r_0 \sigma
\]  

(2)

where \( r_0 \) is the particle radius.

Now, we consider that a solid bridge between two identical spheres is formed by crystallization of the solutes contained in the liquid bridge when the humidity becomes lower. It is assumed that the entire amount \( \left( = N_s (4/3) \pi r_0^3 \right) \), where \( N_s \) is the number of solute molecules divided by the volume of a particle in the liquid bridge) of solute in the liquid bridge forms a solid bridge between particles in a form similar to that of the liquid bridge in Figure 1. This assumption will be discussed later in Result of Experiments. Now, the adhesion force arising from a solid bridge between particles is defined as the force required to break the solid bridge by separation of two particles as shown in Figure 1. We assume that the breakage occurs at \( x = 0 \) in Figure 1, and a relation is derived between the surface area of breakage and the volume of the solid bridge. The volume \( v \) of the bridge in Figure 1 is related to a neck radius \( r_2 \) for the gap between the particles \( h = 0 \) as follows.

\[
v = (\pi/2) r_2^4 / r_0
\]  

(3)

If the above relation exists also in a solid bridge, the surface area \( A_s \) of breakage can be expressed as follows.

\[
A_s = (2\pi r_0 \nu)^{1/2} \times (r_0 \nu)^{1/2}
\]  

(4)

Also, as the volume \( \nu \) of the solid bridge is proportional to the number of solute molecules \( (= N_s (4/3) \pi r_0^3) \), the following equation is obtained from Eq. (4):

\[
A_s \propto \left\{ N_s (4/3) \pi r_0^4 \right\}^{1/2}
\]  

(5)

Here, if the solid bridge is assumed to have uniform strength at any section, because the tensile breakage force is proportional to the sectional area of breakage, the adhesion force \( F_s \) arising from the solid bridge can be expressed by the following formula:

\[
F_s \propto A_s \propto \left\{ N_s (4/3) \pi r_0^4 \right\}^{1/2}
\]  

(6)

Further, if the liquid bridge adhesion force can be obtained by Eq. (2), the following relation is derived from Eqs. (2) and (6):

\[
F_s / F_L \propto N_s^{1/2} r_0
\]  

(7)

If breakage occurs in a solid bridge, it is expected that the relation between the adhesion force arising from a liquid bridge and that of a solid bridge formed by vaporization of water is given by the above formula.

On the other hand, when the amount of soluble salts is reduced, no solid bridge forms in the gap between particles, and the fine crystals are deposited onto the particle surface. In such case, it seems that adhesion force arises from van der Waals force, and the force is smaller than that of the initial liquid bridge. Moreover, if the gap between two particles is increased by deposition of the fine crystal particles in the gap, the van der Waals force becomes even lower.

2. Experimental Method

Glass spheres of 2.5, 5.0 and 7.5 mm in radius were used as particles. In order to form uniform liquid bridges, the glass spheres were dipped in a concentrated hydrochloric acid solution, held by pincers to avoid any contact with hands, washed in flowing ultrapure water, and dried in a thermo-hygrostat (at 298K and 30% humidity) in a clean tunnel. The glass spheres were set-up as shown in Figure 2 so that the centerline of the two spheres coincided with the vertical direction. The glass spheres were set-up as shown in Figure 2 so that the centerline of the two spheres coincided with the vertical direction. Then, liquid bridges of aqueous solution containing solutes \( (2 \times 10 \text{ mol/m}^3 - \text{ultrapure water}) \) were formed between two glass spheres by means of a microsyringe. The liquid bridge volume is \( 2 \times 10^{-5} \text{ m}^3 \). Solutes used in the experiment are NaCl, KCl, KNO_3 and Na_2SO_4, considering that
such ions as Na\(^+\), K\(^+\), Cl\(^-\), NO\(_3\)^{-}, SO\(_4\)^{2-}\) are contained in tap water. The liquid bridge was left in a thermo-hygrostat operated at various constant humidities below the deliquescent points of the salts shown in Table 1 (at a temperature of 289K) until it reached an equilibrium condition (for about 24 hrs). Once the solid bridge was formed in such manner, the glass spheres set as shown in Figure 2 were removed from the thermo-hygrostat, and placed on an electronic balance, as shown in Figure 3. Then, the moving stage was slowly moved downward to separate the two spheres. Readings of the electronic balance were constantly inputted to a personal computer, and the highest reading of the balance at breakage of the solid bridge was taken as the adhesion force of the solid bridge. Although the measurement was carried out in a room at a temperature of 293 to 298K and a relative humidity of 60 to 70%, it took only a few minutes to measure a sample, and it is considered that no change in crystal conditions such as absorption of moisture occurred during the measurement.

| Soluble salt | Critical relative humidity (%) |
|--------------|-------------------------------|
| NaCl         | 76                            |
| KCl          | 84                            |
| KNO\(_3\)     | 92                            |
| Na\(_2\)SO\(_4\) | 83                        |

Table 1 Relative humidity above which salts deliquesce (at 298K)\(^{14}\)

3. Experimental Results and Discussion

Figure 4 shows the measurement results of the solid bridge force. Only 20 points of measurement data are shown for each salt in Figures 4 (a) to (d), because it is a very time-consuming operation to form a solid bridge between two glass spheres as described above. However, the results follow the Weibull distribution, widely distributed within a range of nearly two orders of magnitude. Similar results were obtained under conditions different from those shown in Figure 4 (quantity \(N\) of the salt, radius \(r_0\) of the glass sphere, etc.).

The measurement results are summarized in Figure 5, containing the results of Figure 4. The abscissa represents the amount of crystals (number of molecules) forming the solid bridge multiplied by the radius, which corresponds to the value between braces in the right term of Eq. (6), and the ordinate shows the average value of adhesion forces measured for 20 solid bridges as shown in Figure 4. Although data for individual pieces are distributed within a wide range, the results follow the Weibull distribution graph.

![Figure 3 Experimental set up](image-url)

![Figure 4 (a) Distribution of adhesion force arising from solid bridge formed between two spheres (NaCl)](image-url)
range as shown in Figure 4, the adhesion force \( F_s \) of a solid bridge formed by any of the salts tends to comply with the relation given by Eq. (6). In the case of NaCl in Figure 5 (a), the adhesion force decreases, as the humidity increases when the crystals are formed in the solid bridge. As shown in Table 1, NaCl is deliquescent at a humidity of 76%, and deliquescence of crystals begins at a humidity of 76% when the humidity is increased from a low level. However, water is not completely vaporized even if the humidity is reduced below 76%, although crystals are formed, when the humidity is reduced from a level higher than that level. In this case the water is completely vaporized at a humidity of 30%. Because NaCl has such hysteresis, the results at a humidity of 45 and 60% account for the reduction in the adhesion force due to a small amount of water (undetected by microscopic observation) contained in the crystals. Also, in the case of KCl, a slight difference was found, although it is not as significant as that of NaCl, and it is caused by a hysteresis similar to that of NaCl (KCl is deliquescent at a humidity of 84%, and water is completely vaporized at a humidity of about 45%). In the results of KNO\(_3\) in Figure 5 (c) and Na\(_2\)SO\(_4\) in Figure 5 (d), no difference was detected for different humidities. Since no reference describing the hysteresis of KNO\(_3\) and Na\(_2\)SO\(_4\) was found, changes in weight of the saturated aqueous solution of each salt were examined at various humidities. The hysteresis was not confirmed for both salts within the measurement range. Therefore, the adhesion force for both salts was not affected by humidity as shown in Figures 5 (a) and (d).

Figure 6 shows photographs of a NaCl solid bridge formed between glass spheres. In Figure 6 (a) (before breakage), it is recognized that the profile of the solid bridge is similar to that of the liquid bridge in Figure 1, and the solid bridge is formed so as to fill the gap between the glass spheres. A solid bridge of substantially similar profile was formed in other salts, KCl, KNO\(_3\), and Na\(_2\)SO\(_4\). In Figure 6 (b) (breakage section viewed from above), because the solid bridge has some local voids, and has not a uniform structure, the individual measurement data for adhesive force are distributed within a wide range as shown in Figure 4. Although the adhesive forces
of solid bridges formed by the salts in the experiments are distributed within such range, it is found that Eq. (6) is satisfied by taking the average adhesive force.

A condition for the formation of a solid bridge between glass spheres is that the liquid bridge be kept in an atmosphere at the deliquescent point shown in Table 1 or at a higher humidity. The liquid bridge force $F_L$ can be calculated from Eq. (2). In Figure 7, $F_L$ is compared with the solid bridge force $F_s$ shown in Figure 5. It is clear that the adhesion force of a solid bridge formed by any salt is one to two orders of magnitude larger than that of liquid bridge in high humidities. $F_s/F_L$ agrees with the relation of the Eq. (7) in Figure 7 as well.

In the experiment, the measurement of the adhesion force in a section with a smaller amount of crystals was not achieved, because the solid bridge was broken by a very small force before measurement.
of adhesion force. When the amount of crystals was much smaller, deposits of small crystals on the particle surface were observed, in which the van der Waals force is the main mechanism of adhesion between particles, as described in the Theoretical Discussion. The adhesion force in such state should be studied in the future.

Fig. 6 Photographs of solid bridge (NaCl) formed between two glass spheres

Fig. 7 (a) Ratio of adhesion force arising from solid bridge to liquid bridge force (NaCl) (Keys are the same as those in Fig. 5)

Fig. 7 (b) Ratio of adhesion force arising from solid bridge to liquid bridge force (KCl) (Keys are the same as those in Fig. 5)

Fig. 7 (c) Ratio of adhesion force arising from solid bridge to liquid bridge force (KNO₃) (Keys are the same as those in Fig. 5)
Conclusions

A solid bridge formed after drying a liquid bridge containing such water-soluble salts as NaCl, KCl, KNO₃ and Na₂SO₄ in a low humidity atmosphere, was experimentally studied. The results of the experiments are described below.

1) When a large amount of solutes was contained in an initial liquid bridge, it was found that a solid bridge forms so as to fill the gap between particles, and its adhesion force is one to two orders of magnitude higher than that of the liquid bridge before crystallization.

2) Although the adhesion forces of individual solid bridges were distributed within a wide range, the average value of such forces was proportional to about 1/2 power of the product of the volume of crystals forming the solid bridge and the particle radius. This could be explained by a theoretical model.

3) It was found that the adhesion forces arising from NaCl and KCl bridges increase as the humidity decreases (below their deliquescent points), because they adsorbed water until complete recrystallization took place.

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### Author’s short biography

#### Yasuo Kousaka

The author is Professor of Chemical Engineering Department at University of Osaka Prefecture since 1979. His major research interests are dynamic behavior of aerosol particles, sizing techniques of aerosol particles and powders, and dispersion of aggregate particles in air and water. He is currently editor in chief of Journal of the Society of Powder Technology, Japan, and vice president of Japan Association of Aerosol Science and Technology.

#### Yoshiyuki Endo

The author is Research Associate of Chemical Engineering Department at University of Osaka Prefecture since 1991. His research interests are almost same as those of Professor Kousaka.