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Existence forms of water in solid-liquid systems①

XING Jun(刑 军), LIU Zheng-ning(刘正宁), LI Xin-yue(李昕跃), LIU Rong(刘 荣), HUANG Hui(黄 慧), XU Hai-yan(徐海燕), XU Ji-run(徐继润), REN Shun-nian(任顺年)
(Department of Chemistry and Chemical Engineering, Dalian University, Dalian 116622, P.R.China)

[Abstract] Two approaches, named pressure filtration (PF) and vaporization dewatering (VD), for qualitative and quantitative analysis of the water forms were presented. The principle of VD is that with the process of heating, the free water, surface water and capillary water are in turn vaporized at different rates, then the turning points of the rates are determined and the quantitative analysis can be made. Some experiments with suspension of water and $CaCO_3$ powder were given and discussed by applying the vaporization dewatering approach.

[Key words] solid-liquid separation; existence forms of water; vaporization dewatering
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1 INTRODUCTION

In a solid-liquid system consisting of solid particles and water, there are a series of existence forms of water, such as free water, surface water, capillary water, wrapped water and crystalline water[1]. The free water exists between solid particles (exclude the surface water) can be easily drained by gravity[2]; the capillary water is included in capillary holes on the particle surface and may be dewatered only as the filter pressure is higher than the capillary pressure[3]; the surface water is within the hydrate film on the particle surface[4] and is difficult to be removed in general, but it may be partly replaced by air molecules resolved in water[5,6] or by another kind of liquid[7] when high pressure air or washing liquid is introduced through the solid-liquid system. The internal water is contained within particles and can not be get rid off, unless the particles are ground into smaller ones[2]; as for the crystalline water, it is beyond the scope of solid-liquid separation because it joints with particles by chemical bonds[8].

In general solid-liquid separation, the free water, surface water and capillary water are most important to separation process, and also the primary part to be dewatered. It is easy to understand that the different forms of water in a solid-liquid separation need to be dewatered by different approaches. So that the qualification and quantification determination of the water forms in a solid-liquid system is rather essential to the selection of separation methods and the prediction of process efficiency. However, in a long period effective method has not been developed to determine the quantitative composition of the various forms of water in solid-liquid system. In this paper, the authors present two approaches to the problem: one is the pressurized filtration approach (PF), the other is the vaporization dewatering approach (VD); also the theoretical bases of the two methods are discussed, but only the latter is verified experimentally.

2 THEORETICAL ANALYSIS

Taking into account the fact that some forms of water in a solid-liquid system are easy to be removed and others are difficult, two approaches to the qualitative and quantitative analysis of the water forms are presented as follows.

2.1 Pressure filtration approach

The principle of the pressure filtration approach is shown schematically in Fig.1. Because the free water is easier to be rejected than capillary water and surface water under pressure filtration, when increasing the filter pressure, the residual water in the solid-liquid system will be varied with filtration time as displayed by the broken line in Fig.1. This broken line represents the different dewatering stages of different forms of water, the line slopes are the corresponding dewatering rate. It is noted that due to the limited pressure applied in filtration an equilibrium stage will be reached at last where the residual water does not change, as shown by the 4th stage in Fig.1. Fig.1 indicates that if such broken line is obtained experimentally, the qualitative and quantitative determination of different forms of water become possible.

The principle of the filtration approach is beyond doubt, but the operation is difficult because the successive increase of filter pressure is impossible in prac-

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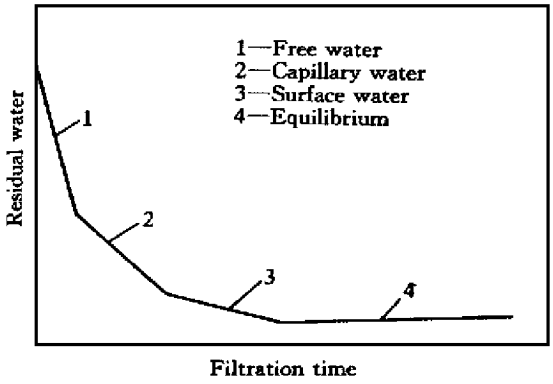

Fig.1 Principle of pressure filtration approach

tice. One can only enhance the pressure continuously. During the transitional period between two pressure levels, the dewatering rate will not be constant. This is why the pressure filtration method is not used in our experiments.

2.2 Vaporization dewatering approach

The vaporization dewatering approach is based on the following fact that the water molecules subjected the least restriction of solid particles will be vaporized firstly, then the less bounded molecules remove, the molecules most close to the solid surface should be got rid of at last. Therefore, with the extension of heating time, firstly the free water, then the surface water, finally the capillary water are vaporized, the decreasing trend of the residual water in solid-liquid system is shown schematically in Fig.2. The surface water is supposed to be removed easier than capillary water because the vaporization rate should be directly proportional to the heated area[8]. On the particle surface, the section area of capillary holes is obviously a very small part of the total surface. As a result, the surface water is vaporized prior to the capillary water.

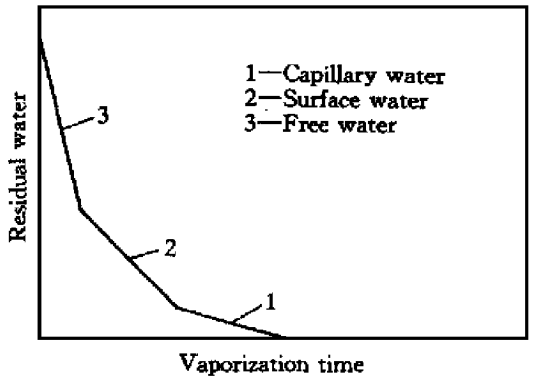

Fig.2 Principle of vaporization dewatering approach

In addition, it should be noted that compared with Fig.1, there is no equilibrium stage in Fig.2. This is because the residual water can be reduced to zero if the heating time is long enough.

The vaporization dewatering approach is convenient to be operated and utilized in this paper to analyze the existence forms of water both qualitatively and quantitatively.

3 RESULTS AND DISCUSSION

The experimental results of a solid-liquid system composed of $CaCO_3$ powders, with average diameter of 10 μm calculated by using specific surface area, are given in Fig.3. The experiments are carried out with a Microwave Moisture Quick Analyzer. At the beginning stage (about 3 min), the residual water decreases gradually, the vaporization rate is low. This is apparently due to the low system temperature, the heat absorbed by water molecules is not high enough to result in stable vaporization. Therefore this stage should be excluded when the vaporization rate is calculated. As expected, the time needed to vaporize water molecules decreases with the reduction of the original water content.

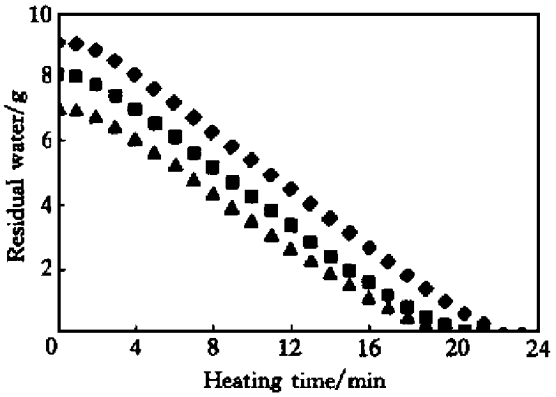

Fig.3 Residual water as a function of heating time at heating temperature of 60 ℃
◆—1 g $CaCO_3$ + 9 g H_2O; ■—2 g $CaCO_3$ + 8 g H_2O;
▲—3 g $CaCO_3$ + 7 g H_2O

Always there is a transition area between two vaporization stages, in this area the vaporization changes from one rate gradually to another and no obvious transition point can be seen, as shown by Fig. 1. This can be explained as follows. In practical vaporization, it is impossible for the first surface water molecule to escape provided that the last free water molecule is vaporized; in other words, around the boundary point of two stages two kinds of water molecules are liberated from the solid-liquid system at the same time, which results in the transition zone as seen in Fig.3. Because the boundary of the two vaporization stages can not be seen directly from the experimental results, it should be determined by graphic method, i.e. one need to draw two lines which represent the vaporization rates of two neighbor stages and their intersect point indicates the boundary.

The quantitative composition of the free water, surface water and capillary water in the solid-liquid system can be determined by graphic method. The

principle of the method is demonstrated in Fig.2. For example, using the data curves in Fig.3, draw three lines across the data points of each curve, where each line has its individual slope (similar to that of Fig.2) are obtained, the vaporizing time and the residual moisture of each transitional point are read directly. The vaporization rates in different stages can also be easily calculated.

The data listed in Table 1 are obtained from graphic methods (when calculate the vaporization rate of free water, the preheating time has been excluded, but still included in vaporization time). The results shows that the quantities of surface and capillary water are almost proportional to the concentration of the system.

Table 1 Distribution of various water

	1 g $CaCO_3$ + 9 g H_2O			2 g $CaCO_3$ + 8 g H_2O			3 g $CaCO_3$ + 7 g H_2O		
	Free water	Surface water	Capillary water	Free water	Surface water	Capillary water	Free water	Surface water	Capillary water
Vaporization time/min	19.5	3.5	1.0	16.2	4.5	1.3	13.0	6.7	2.3
Quantity/g	8.1	0.85	0.05	6.5	1.4	0.1	4.85	2.0	0.15
Percentage	86.9	9.3	3.8	81.3	17.5	1.25	69.3	28.5	2.2
Vaporization rate/(g·min^{-1})	0.46	0.24	0.05	0.47	0.31	0.08	0.43	0.30	0.07

4 CONCLUSIONS

1) The existence forms of water in solid-liquid systems are very significant to the selection of solid-liquid separation methods and the prediction of the process efficiency. But there has not yet a suitable approach which can be used for the qualitative and quantitative determination of the water forms. In this paper, we present two approaches, especially the vaporization dewatering, to the problem mentioned above.

2) The existence forms of water in a solid-liquid system containing $CaCO_3$ and water are measured and discussed by using the heating dewatering approach, and it is proved that the method is effective for the qualitative and quantitative analysis of water forms in the system.

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