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Distribution of aluminum species and the characteristics of structure of poly-aluminum-chloride-sulfate (PACS)

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Abstract: A series of poly-aluminum-chloride-sulfate (PACS), which has different basicities (γ) and Al^{3+}/SO_4^{2-} molar ratio, has been prepared and dried at 105℃ and 65℃, respectively. The distribution of aluminum species of PACS was examined, and the effect of γ value, Al^{3+}/SO_4^{2-} molar ratio, dilution on the distribution of aluminum species of PACS was also investigated by using Al-ferron timed complex colorimetric method. The IR spectroscopy and X-ray diffraction were used to study the effect of γ value, Al^{3+}/SO_4^{2-} molar ratio and the drying temperature on the structure of PACS. The experimental results show that Al^{3+}/SO_4^{2-} molar ratio has a great effect on the distribution of aluminum species, but the dilution has a little effect on the distribution of aluminum species. The lower the Al^{3+}/SO_4^{2-} molar ratio, the higher the proportions of the polymer and colloidal species in PACS. The polymeric degree of PACS was related to γ value and Al^{3+}/SO_4^{2-} molar ratio. Drying temperature has an influence on the structure and the solubility of solid PACS products.

Key words: flocculant PACS; species; structure; Al-ferron timed complex colorimetric method; IR spectroscopy; X-ray diffraction

Introduction

Polyaluminum chloride (PAC), which was developed in the 1960's in Japan, has come to be used extensively in place of aluminum sulfate in water and wastewater treatment because of its ability to achieve adequate aggregation even at low temperatures and to form flocs relatively rapidly (Tang, 1995; Yao, 1989; Dempsey, 1985). Recently, PAC has been reported to be an effective flocculant for removal of inorganic anions, such as phosphate, fluoride, organic micropollutants.

In order to improve the coagulating effect and the quality of PAC, higher polymerized PAC should be developed. The polymeric degree of PAC can be increased by adding more base during the preparation of PAC to increase the OH/Al molar ratio which is often expressed as γ (in this paper, γ was used as standing for OH/Al molar ratio). However, a major problem associated with the use of higher γ value of PAC is the stability of the PAC solution. The difficulty is that aqueous solutions of higher γ value of PAC tend to form a precipitate of aluminum hydroxide or become cloudy or partly gelatinous after only a short period of time. When this occurs, these solutions can no longer be used or are less effective in coagulation/flocculation.

Another way to develop higher effective polyaluminum salts is by introducing some multivalent inorganic anions into PAC solution during the preparing process of PAC. It was also found that sulfate ion is the best choice (Gao, 1994). The mixed inorganic polymer flocculant made by adding sulfate ion into PAC solution, poly-aluminum-chloride-sulfate, is often called PACS. In PACS products, the amount of sulfate ion added was expressed as Al^{3+}/SO_4^{2-} molar ratio. Here, it must be pointed out that Al^{3+}/SO_4^{2-} molar ratio mentioned is the added Al^{3+}/SO_4^{2-} molar ratio, and I am not sure if all added sulfate ions play a role in increasing the polymeric degree of PAC. The mechanism of increasing polymerization degree of PAC by adding sulfate ion has not been proved accurately yet, and it is postulated that the PAC polymers are linked through hydrogen bonds.

This paper mainly considers the distribution of aluminum species and the characteristics of structure of PACS as a flocculant. A few points of view are given as well. For PACS samples prepared in my study, the γ and Al^{3+}/SO_4^{2-} molar ratio are varied from 0.5 – 2.5 and 8.0 – 20 respectively.

1 Experimental procedures

Flocculants PACS with different γ value and Al^{3+}/SO_4^{2-} molar ratio were prepared in our laboratory by the following procedure: dissolve quantitative $AlCl_3 \cdot 6H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$ by adding quantitative distilled water and heating after having been mixed up. Another solution, which should prepared by dissolving quantitative Na_2CO_3 in distilled water after heating, is poured into the former solution in batches. Stir the mixture till no bubble comes out and the solution becomes clear enough. The total concentration of Al (III) in PACS solution is expressed as Al_T. It should be point out that the PACS samples of $Al^{3+}/SO_4^{2-} = \infty$ and different γ value are PAC samples. The distribution of aluminum species of PACS was determined by a timed colorimetric method. The structural characterization of PACS was examined by using X-ray diffraction technique and the infrared (IR) spectra measurement method.

2 Results and discussion

2.1 The distribution of aluminum species of PACS solutions determined by a timed colorimetric method

A timed complex-colorimetric analysis procedure with ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) reagents was used to analyze the distribution of aluminum species of PACS solutions (Parthasarathy, 1985).

The absorbances of the Al(III)-ferron complexes are directly determined by a Varian DMS 100S model spectrophotometer. The distribution of the various species in the PACS solutions ($Al_T = 0.1$mol/L) are estimated from the absorbance as a function of time and the typical result is given in Fig.1.

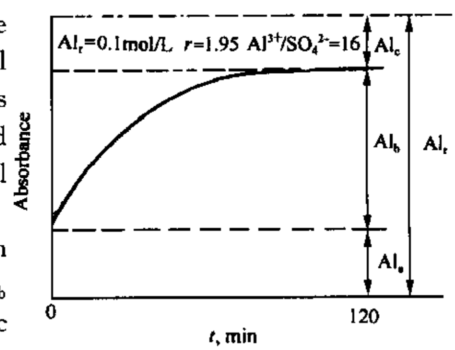

Fig.1 Curve for reaction of PACS with ferron

According to the rate of the reaction, as shown in Fig.1, three kinds of aluminum species denoted Al_a, Al_b and Al_c can be divided by using timed spectrophotometric method (Luan, 1990). Al_a is assumed to include the free Al^{3+} ion, monomers such as $Al(OH)^{2+}$, $Al(OH)_2^+$ and dimers such as $Al_2(OH)_2^{4+}$. The species which reacted with ferron during 120 min are considered to be Al_b, which is assumed to be the active part of hydroxyl aluminum polymers like $Al_3(OH)_5^{4+}$, $Al(OH)_6^{6+}$, $Al(OH)_{16}^{8+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and so on. Al_b is characterized by middle-sized polymerization degree and higher positive charge. The species that do not react with ferron before 120 minutes are considered to be Al_c($Al_c = Al_T - Al_a - Al_b$), which is assumed to be the inert part of high polymers and fresh precipitates like $Al(OH)_3$(am). The proportion of these species depend on the factors such as A_T, γ value, Al^{3+}/SO_4^{2-} molar ratio, and aging time and so on.

2.1.1 The effect of Al^{3+}/SO_4^{2-} molar ratio and γ value on the distribution of aluminum species in PACS solution

The changes of concentration for three groups of species in PACS solution with Al_T = 0.1 mol/L as a function of Al^{3+}/SO_4^{2-} molar ratio and γ value are calculated and summarized in Table 1.

Table 1 showed that (1) under the condition of fixed Al^{3+}/SO_4^{2-} molar ratio, the pattern of the change of Al_a, Al_b and Al_c with γ value in PACS solutions is the same as that in PAC solutions. Al_a decreases gradually with the increase of γ value, but Al_b and Al_c increase gradually with the increase of γ value. (2) When γ value is fixed, the contents of Al_a, Al_b and Al_c vary with Al^{3+}/SO_4^{2-} molar ratio. Al_a and Al_b decrease gradually with the decrease of Al^{3+}/SO_4^{2-} molar ratio. However, Al_c increases gradually with the decrease of Al^{3+}/SO_4^{2-} molar ratio. The higher the γ value, the more evident the change of Al_b and Al_c with Al^{3+}/SO_4^{2-} molar ratio. In comparison with PAC, PACS is less in Al_a and Al_b, but more in Al_c.

Table 1 Effect of Al^{3+}/SO_4^{2-} molar ratio and γ value on the distribution of Al species in PACS solution

γ value	Al^{3+}/SO_4^{2-} molar ratio	Al_a, %	Al_b, %	Al_c, %
0.5	∞	71.85	20.32	7.83
	24	70.18	19.80	10.02
	20	68.28	19.30	12.42
	16	66.10	19.00	14.90
	12	65.80	18.40	15.80
	8	64.80	17.47	17.73
1.0	∞	56.78	31.10	12.12
	24	56.53	25.87	17.60
	20	54.50	25.63	19.88
	16	52.50	25.12	22.38
	12	52.50	24.40	23.10
	8	51.02	22.39	26.59
1.5	∞	38.10	39.80	22.10
	24	37.33	38.57	24.10
	20	36.82	37.05	26.13
	16	36.58	35.35	28.07
	12	34.60	31.35	34.05
	8	34.08	25.38	40.54
2.0	∞	20.91	49.55	29.54
	24	20.65	47.28	32.07
	20	19.65	42.28	38.07
	16	19.43	36.06	44.52
	12	19.65	34.30	46.05
	8	18.90	30.60	50.50
2.5	∞	9.49	55.48	35.03
	24	8.82	52.95	38.23
	20	8.47	52.50	39.03
	16	7.98	43.04	48.98
	12	7.47	40.55	51.98
	8	7.22	30.86	61.92

It is also seen from Table 1 that the smaller the Al^{3+}/SO_4^{2-} molar ratio (i.e. the more the content of sulfate ion in polyaluminum solution), the more evident the differences in the content of the aluminum species between PACS and PAC. This means that incorporating sulfate ion into basic polyaluminum salts effects the distribution of aluminum species in polyaluminum salts. There should exist an appropriate Al^{3+}/SO_4^{2-} molar ratio, otherwise, incorporating more sulfate ion into polyaluminum salts will result in the formation of some precipitates which phenomenon can be observed during the preparation of PACS products (Dehe, 1978).

Since the Al_a and Al_b are cationic species, they can make colloidal particles destabilize and aggregate by charge-neutralization. The species Al_c can make colloidal particles aggregate by bridging because of its high polymer. Since the contents of Al species in PACS solution are affected by Al^{3+}/SO_4^{2-} molar ratio, the coagulation effect and mechanism of PACS in water and wastewater treatment will be affected by Al^{3+}/SO_4^{2-} molar ratio. According to my research on the properties, efficiency and application of PACS in water and wastewater treatment, an appropriate molar ratio of Al^{3+} to SO_4^{2-} should be in the range of 15 – 17.

2.1.2 The effect of dilution in water on the distribution of aluminum species in PACS solution

The PACS samples which have different γ value and $Al^{3+}/SO_4^{2-} = 16$ or ∞ were taken as examples to investigate the effect of dilution in water on the distribution of aluminum species in PACS solution. First of all, the samples were diluted 50 or 100 times with distilled water, then, aged for 5 hours, and finally, the contents of aluminum species were determined by the timed colorimetric method. The experimental results are shown in Table 2. It is found from Table 2 that the dilution has a little effect on the distribution of Al species both in PACS solution and PAC solution. Under the condition of the γ value below 2.0, the tendency of Al species change is about the same both in PACS and PAC. The content of Al_a increases slightly with dilution, but the contents of Al_b and Al_c decreases slightly with dilution. When the γ value is equal to or more than 2.0, the contents of aluminum species both in PACS solution and PAC solution keep roughly stable. Since the behavior of coagulation/flocculation of aluminum salts has the close relation to the aluminum species, the coagulating effect of PACS in water and wastewater treatment will not change with dilution, which advantage can meet the requirement of water and wastewater treatment for flocculants.

Table 2 Effect of dilution on the distribution of aluminum species in polyaluminum solutions

γ value	Sample	$Al_T = 1.0 \times 10^{-1}$ mol/L			$Al_T = 2.0 \times 10^{-3}$ mol/L			$Al_T = 1.0 \times 10^{-3}$ mol/L		
		Al_a, %	Al_b, %	Al_c, %	Al_a, %	Al_b, %	Al_c, %	Al_a, %	Al_b, %	Al_c, %
0.5	PAC	71.85	20.32	7.83	74.99	17.51	7.50	76.70	16.10	7.20
	PACS	66.10	19.00	14.90	71.42	16.08	12.50	70.42	16.67	12.91
1.0	PAC	56.78	31.10	12.12	59.52	29.11	11.37	61.57	27.37	11.06
	PACS	52.50	25.12	22.38	54.26	24.90	20.84	54.25	24.41	21.30
1.5	PAC	38.10	39.80	22.10	37.54	39.06	23.35	37.58	38.57	23.83
	PACS	36.82	37.05	26.13	37.83	29.62	30.57	39.32	26.87	33.81
2.0	PAC	20.91	49.55	29.54	19.68	47.77	32.55	19.66	49.76	30.50
	PACS	19.43	36.06	44.52	21.49	38.23	40.23	22.40	37.82	39.78
2.5	PAC	9.49	55.48	35.03	8.75	55.46	35.29	10.74	54.94	34.32
	PACS	7.98	43.04	48.92	5.74	46.77	47.49	5.49	47.26	47.25

2.2 The characterization of the chemical structures of the solid polyaluminum samples by *X*-ray diffraction

In order to obtain solid form polyaluminum samples, the polyaluminum solutions ($Al_T = 2.0$ mol/L) of $\gamma = 1.9$ and $Al^{3+}/SO_4^{2-} = 16$ or ∞ were dried by two methods: the one is to dry the solutions in a vacuum oven at 65 ℃; the other one is to dry the solutions in a non-vacuum oven at 105℃. Then, the solid samples were examined by using a D/max-γA model diffractometer to study the effect of drying temperature on the structural characteristics of the solid samples. The results are given in Fig.2 and Fig.3 respectively. The results showed that the drying temperature

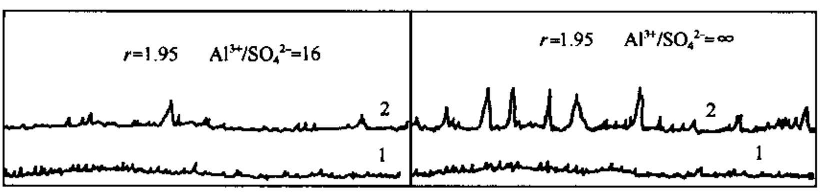

Fig.2 Effect of drying temperature on the *X*-ray diffraction of PACS at $\gamma = 1.95$
(1) $T = 65$℃; (2) $T = 105$℃

affects the structure of solid PACS and PAC samples. Both the solid PACS of $\gamma = 1.95$ and $Al^{3+}/SO_4^{2-} = 16$ and the solid PAC of $\gamma = 1.95$ and $Al^{3+}/SO_4^{2-} = \infty$ obtained in the vacuum oven at 65℃ do not appear any obvious diffraction peaks, which means that they possess amorphous structures and have a good solubility in water. In Fig.3, the upper *X*-ray diffraction spectrum with sharp peaks represents the solid PAC sample of $\gamma = 1.95$ and $Al^{3+}/SO_4^{2-} = \infty$ dried at 105℃ and the below one with few peak represents the solid PACS sample of $\gamma = 1.95$ and $Al^{3+}/SO_4^{2-} = 16$ dried at 105℃. The pattern shows that two samples have different structures. The solid PACS sample without a characteristic diffraction peak possesses amorphous structure, and has a good

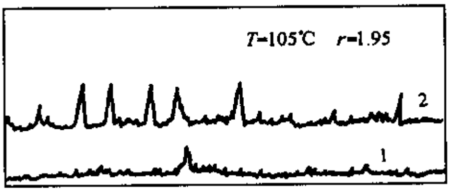

Fig.3 Effect of the molar ratio of Al^{3+}/SO_4^{2-} on the X-ray diffraction of PACS
(1) Al^{3+}/SO_4^{2-} = 16; (2) Al^{3+}/SO_4^{2-} = ∞

solubility in water. However, the solid PAC sample with obvious diffraction peaks may possess the gibbsite crystalline structure and is not as soluble in water as amorphous structure of PACS. It is concluded from above results that drying temperature has a greater effect on the structure and the solubility of PAC than on those of PACS. Incorporating a low level of sulfate ions into basic polyaluminum salts was beneficial with respect to their solubility, especially for the solid polyaluminum samples dried at higher temperature. It is common knowledge that the coagulation effect of flocculants will be weakened if they do not have a good solubility in water. So, the solid PACS products dried at higher temperature should give better performance than solid PAC products dried at higher temperature in water and wastewater treatment.

2.3 The characterization on the chemical structures of the solid polyaluminum samples by infrared (IR) spectroscopy

Infrared (IR) spectra of solid PACS samples (Al_T = 2.0 mol/L) having different γ value and Al^{3+}/SO_4^{2-} molar ratio were measured by a Nicolet 5DX FT-IR spectrophotometer, using a 4/cm resolving power and a scanning frequency of 60. The PACS samples were laminated by using KBr as mother substance, and the weight ratio of the PACS sample to KBr was 1:35. The results were given in Fig.4 and Fig.5, respectively. It is seen from the spectra that there are several adsorption bands. The main ones of them are the high-frequency band at 3420 – 3450/cm, the medium-frequency band at 1630/cm, and the low-frequency bands at 1105/cm and at about 613/cm, respectively. Since the expending and contracting vibration of the hydroxyl is in between 3000 – 3700/cm, the high-frequency band at 3420 – 3450/cm is assignable to the hydroxyl groups directly bound to the Al ions in polyaluminum and the hydroxyl groups of water molecular existed in solid polyaluminum products. The medium-frequency bands observed at 1630/cm may attribute to the hydrogen bond of water molecular attached to solid polyaluminum products to form hydronium. The low-frequency band observed at about 1105/cm may be assignable to the expending and contracting vibration of Al—O(H)—Al of the polyaluminum products. The low-frequency bands observed at about 613/cm may be the bending vibration of Al-OH groups located on the edges of the polyaluminum salts (Farmer, 1974). Since there existing water in the solid polyaluminum salts, it may be reasonable that the adsorption bands at 1105/cm and 613/cm are taken as the characteristic adsoption bands to directly characterize the polymeric degree of the solid PACS polymer. The stronger the adsorption bands at 1105/cm and 613/cm, the higher the degree of the polymerization of polyaluminum salts. Generally speaking, the higher the polymeric degree of the polymers, the better the coagulating effect of them, because the higher polymers perform stronger bridge- formation ability for colloidal particles in water. It is seen from Fig.4 and Fig.5 that strength of the adsorption bands at 1105/cm and 613/cm changes with the change of γ value and Al^{3+}/SO_4^{2-} molar ratio of the solid polyaluminum samples dried both at 65℃ and 105℃. In order to understand the change well, we can compare the change of the integral areas of the adsorption bands at 1105 /cm and 613/cm. The integral areas of peak at 1105/cm are shown in Table 3. It is found from Table 3 that the polymeric degree of PACS is related to Al^{3+}/SO_4^{2-} molar ratio and γ value. The higher the γ value, the larger the integral areas, which means that the polymeric degree of PACS increases with the increase of γ value. However, we should bear in mind that γ value should not be too high, otherwise, the aqueous solution of PACS tend to form a precipitate of $Al(OH)_3$, which will reduce its coagulation effect.

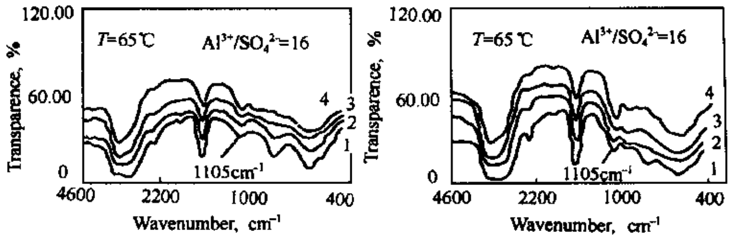

Fig.4 Effect of γ value on the infrared spectrum of PACS
(1)$\gamma=0.5$; (2)$\gamma=0.9$;(3)$\gamma=1.5$;(4)$\gamma=1.95$

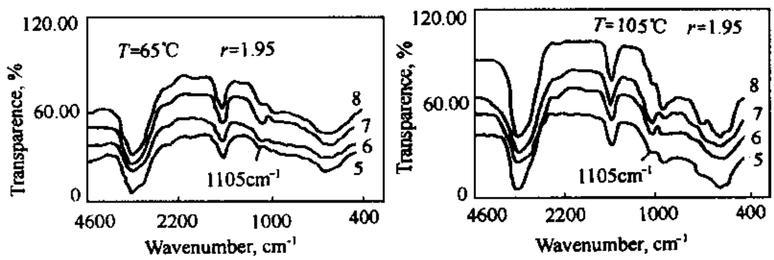

Fig.5 Effect of the Al^{3+}/SO_4^{2-} molar ratio on the infrared spectrum of PACS
(5)$Al^{3+}/SO_4^{2-}=8$;(6)$Al^{3+}/SO_4^{2-}=12$;(7)$Al^{3+}/SO_4^{2-}=16$;(8)$Al^{3+}/SO_4^{2-}=\infty$

Table 3 The integral area of the peak at 1105/cm

Drying temperature	γ value	Al^{3+}/SO_4^{2-} molar ratio	Integral area	Drying temperature	γ value	Al^{3+}/SO_4^{2-} molar ratio	Integral area
65℃	0.5	16	3.28	105℃	0.5	16	12.04
	0.9	16	4.17		0.9	16	12.97
	1.5	16	6.31		1.5	16	15.06
	1.95	16	9.39		1.95	16	17.53
	1.95	8	2.89		1.95	8	4.92
	1.95	12	4.74		1.95	12	10.92
	1.95	16	9.39		1.95	16	17.53
	1.95	∞	2.43		1.95	∞	3.76

It was also found that when the Al^{3+}/SO_4^{2-} molar ratio is in the range of 8 – 16, the higher the Al^{3+}/SO_4^{2-} molar ratio, the larger the integral areas, which means that the polymeric degree of PACS increases with the increase of the Al^{3+}/SO_4^{2-} molar ratio. In comparison with PACS samples, PAC of $Al^{3+}/SO_4^{2-}=\infty$ gives the smallest integral area, which means that incorporating a low level of sulfate ions into basic polyaluminum salts was beneficial with respect to the increase of their polymeric degree and their performance as flocculants.

3 Conclusions

Based on the results of this paper, the following conclusions are made.

The experimental results obtained by IR show that the polymerization degree of PACS has a close relation with its γ value. The polymerization degree of PACS increases with the increasing of γ value.

The experimental results obtained by timed colorimetric method show that Al^{3+}/SO_4^{2-} molar ratio and γ value have a great effect on the distribution of aluminum species of PACS solutions. In comparison with PAC, PACS is less in Al_a and Al_b, but more in Al_c. Dilution has a little effect on the distribution of aluminum species. Because the performance of PACS as flocculant has a close relation with aluminum species, the coagulating effect of PACS will be affected by the γ value and Al^{3+}/SO_4^{2-} molar ratio of PACS too.

Drying temperature has a greater effect on the structure and the solubility of PAC than on those of PACS. Incorporating a low level of sulfate ions into basic polyaluminum salts was beneficial with respect to their solubility, especially for the solid polyaluminum samples dried at higher temperature. In comparison to the solid PAC product with the gibbsite crystalline structure, the solid PACS product possessing amorphous structure, which results in good solubility in water, should give better performance as flocculant.

For the sake of developing further inorganic polymer flocculant, many aspects, such as their coagulation efficiency, special mechanisms of flocculant and flocculation, and optimum production technology, still remain to be researched.

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