Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1044917

57 (2016) 11789–11799
May

Taylor & Francis
Taylor & Francis Group

Effect of aluminum speciation on silica removal during coagulation of heavy-oil wastewater using polyaluminum chloride

Xiaofei Zhao[a,*], Tengfei Yang[a], Lixin Liu[a], Xiaoyang Zhang[a], Lei Fan[a], Youquan Huang[b]

[a]*College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing 163318, China, Tel. +86 459 650 4061, +86 138 0469 0525; email: dqpifxz@163.com (X. Zhao), Tel. +86 151 6457 5980; email: yangmo575@163.com (T. Yang), Tel. +86 138 0469 0527; email: lxliu68@163.com (L. Liu), Tel. +86 152 4595 5780; email: 15245955780@163.com (X. Zhang), Tel. +86 183 4597 7615; email: 371719833@qq.com (L. Fan)*
[b]*Daqing Oilfield No. 5 Oil Production Plant Company Ltd, Petrochina, Daqing 163513, China, Tel. +86 459 459 5377; email: huangyouquan@petrochina.com.cn*

Received 9 October 2014; Accepted 18 April 2015

ABSTRACT

Desiliconization techniques for heavy-oil wastewater are complex and costly. The effect of polyaluminum chloride (PACl) on silica removal during coagulation, however, has not been examined. In this study, the effect of PACl on the removal of soluble silica in heavy-oil wastewater was investigated by analyzing the major species of silica and aluminum during various stages of coagulation. Soluble silica could be divided into three species based on increasing molecular weight: monomer and dimer (Si_a), oligomer (Si_b), and polymer (Si_c). Likewise, aluminum hydrolysates could be divided into the species Al_a, Al_b, and Al_c, which correspond to oligomers of increasing molecular weight. Three PACl samples of specific basicities synthesized in our laboratory, with Al_a, Al_b, and Al_c being dominant in one of the samples, were used. Aluminum salts and preformed collosols of amorphous aluminum hydroxide were employed to explore the effect of Al_a and Al_c on soluble silica in wastewater. Results show that Al_a and Al_c promoted the removal of Si_c and Si_a, respectively. The interaction of Si_c and Si_a with Al_a and Al_c, respectively, can be described as absorption-modification, causing the formed admixtures of silica and aluminum to become more insoluble and more susceptible to coagulation. A mechanism involving electrostatic patch coagulation is introduced to explain the reaction of soluble silica and other substances with PACl.

Keywords: Heavy-oil wastewater; Soluble silica; Aluminum hydrolysates; Absorption-modification; Aluminosilicate sites

1. Introduction

Steam flooding, a widely used procedure in the exploitation of heavy oil [1,2], promotes hydrolysis of silica-rich rocks in oil reservoirs [3,4], leading to the high silica content of heavy-oil wastewater [5,6]. Most of the treated wastewater is reused in boilers [7]. Standards for water quality have been in place to strictly control formation and deposition of silica scale in boilers. According to the Chinese Standard SY0097-2000

---

*Corresponding author.

[8], the silica concentration in wastewater should be reduced to <50 mg/l. However, meeting this requirement is difficult in some regions in China because of the lack of resources for specialized techniques such as membrane treatment for desiliconization. Consequently, silica scale formation in boilers continues to be a serious problem [9,10], leading to safety hazards and thermal wastage [11,12]. Hence, the removal of silica in heavy-oil wastewater should be prioritized.

Chemical methods such as precipitation and coagulation are the major techniques for silica removal. They use metal salts, metal oxides, or metal hydroxides of magnesium, calcium, aluminum, and iron [1,13–16]. Lime and magnesium hydroxide are efficient at desiliconization [5,17–19], but their processes require an independent clarifier after flocculation [20] as well as water softening. In contrast, aluminum compounds, especially aluminum salts, have been widely used as coagulants, as they are also efficient at silica removal for brackish and geothermal waters [21,22]. They simplify removal and mitigate most of its adverse effects. Polyaluminum chloride (PACl), which contains a preformed polymerized species, is particularly efficient and useful [23,24] compared with aluminum salts. Thus, it may be the most popular coagulant for oil-contaminated wastewater. Many investigations have focused on the removal of oil, suspended solids, and chemical oxygen demand with PACl [25–27]. However, discussions on the mechanisms of removal of various silica species from wastewater using aluminum hydrolysis products are few.

To explore the interactions between substances in wastewater, we sought to classify and analyze them. Silica species in water have been classified using various criteria, including degree of polymerization and particle size [28,29]. They may be divided into three species based on increasing molecular weight: monomer and dimer (Si_a), oligomer (Si_b), and polymer (Si_c) as measured by color-development times in the molybdate assay [30,31]. Recently, flame atomic absorption spectroscopy, attenuated total reflectance Fourier transform infrared spectroscopy, capillary zone electrophoresis, X-ray diffraction, and spectrophotometry have been used to determine silica species [32–36]. Nevertheless, the molybdate colorimetric assay remains the standard method for determination of silica species. The total concentration of silica may be obtained conveniently and accurately by hydrofluoric acid (HF) transformation method [37,38]. Ferron method and ^{27}Al nuclear magnetic resonance (NMR) spectroscopy were performed for definitive analysis of aluminum species [39–41]. The ferron method divides aluminum species of PACl aqueous dispersions into three fractions, namely mononuclear aluminum (Al_a), reactive polynuclear aluminum (Al_b), and inert or colloidal aluminum (Al_c), which represent oligomers of increasing molecular weight, as measured by colorimetric assay. This method is simpler and less expensive compared with ^{27}Al NMR spectroscopy. A modification of the ferron method that is based on k value analysis has improved precision and repeatability over the original ferron method [42].

More studies on silica removal have been done on aluminum salts than on PACl. Iler [43] discovered that adsorption of even much less than a monolayer of aluminum ions on the surface of amorphous silica could reduce the equilibrium solubility of silica. The removal efficiency of colloidal silica by alumina is much higher than that achieved with reactive silica [18]; ~1 mol of Al^{3+} results in removal of 40 mol of colloidal silica. Many studies have shown the coagulation properties of aluminum coagulants in the presence of silicic acid in terms of flocculation efficiency and floc strength, as well as their reaction mechanism and applicability [44–48]. Negatively charged polymeric silicic acid could combine with aluminum and its hydrolysis products to form a hydrolyzed complex of silica–aluminum species that may enhance the bridge adsorption effect of polyaluminum silicate chloride [46]. Polymer silicic acid is more effective than is monomeric silicic acid in binding mononuclear aluminum, as it forms soluble aluminosilicates [49]. Wang et al. [50] proposed that such binding induces a significant increase in levels of mononuclear aluminum and soluble aluminum in water, thus affecting aluminum speciation. Known mechanisms of coagulation are mainly charge neutralization and sweep flocculation [51]. Both explain desiliconization during flocculation, although the former mechanism is not yet entirely understood. A model for precipitation charge neutralization [52] apparently applies to aluminum salt coagulants. Wang et al. [53] proposed the process of electrostatic patch coagulation (EPC) to interpret the coagulation behavior of PACl enriched in positively charged polymeric aluminum.

In the present work, continuous variations of major species of silica and aluminum were investigated using commercially available PACl and PACl synthesized in our laboratory. The interaction among these species apparently led to their lowered solubility. Silica removal is an important but not separate process of coagulation; hence, the coagulation mechanism of EPC was introduced to gain better insight into the entire removal process.

2. Materials and methods

2.1. Laboratory instruments and chemicals

An ultraviolet spectrophotometer (UV-8000, Metash instrument Co., Ltd, China) and quartz cuvettes were used for measurements on silica speciation and aluminum speciation. pH values were determined using an acidometer (PHS-3C, INESA Scientific Instrument Co., Ltd, China). Coagulation experiments were conducted with a six-joint heat-collection constant-temperature magnetic stirrer (HJ-6, Changzhou ZOJE Experimental Instruction Manufacturing Co., Ltd, China). Vessels for reaction and storage consisting of high-density polyethylene (HDPE) were used to avoid contamination encountered with the use of glass containers.

Aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$), sodium hydroxide (NaOH), hydrochloric acid (HCl), HF, oxalic acid ($H_2C_2O_4$) and acetone (CH_3COCH_3) were of analytical grade. A stock solution of ammonium molybdate was freshly prepared each day of the experiment [31], and the ferron solution [42] for colorimetry was prepared every 5 d. Double-deionized water was used for both reagents. PACl containing 30% Al_2O_3 was obtained from Shandong Taihe Water Treatment Co., Ltd, China. PACl synthesized in the laboratory was prepared according to a procedure in the literature [40]. Both PACl samples were used to determine the effect of coagulation on silica removal. Collosols of amorphous aluminum hydroxide at pH 7 were freshly prepared by immediate blending of a certain amount of $AlCl_3{\cdot}6H_2O$ and NaOH and then filtered through 0.45-μm filters. Samples of heavy-oil wastewater were provided by Liaohe Oil Field.

2.2. Experimental procedure

Batch coagulation experiments using magnetic stirrers (HJ-6) were conducted at 70℃, based on the practical operating temperature of pilot plant in Liaohe Oil Field. To initiate an experiment, a total amount of 800 ml wastewater was equally divided into four HDPE beakers, and 200 ml of pure water with the same pH was prepared. After the above solution was rapidly heated to 70℃, the procedures were as follows: Three parallel samples and the pure water were stirred, respectively, at 200 rpm for 5 min after coagulant addition, and then the timer was started till the mixtures were settled for regularly sampling within next 2 h. The rest wastewater sample was set as blank experiment. Subsamples were drawn at ~2 cm below the liquid level and immediately analyzed. Initial speciation of aluminum was analyzed through the aforesaid pure water, and initial speciation of silica was analyzed through the blank wastewater. Every experiment was repeated more than twice.

2.3. Analytical methods

Wastewater subsamples were filtered through 0.45-μm filters to determine the concentration of soluble silica that was equal to the total silica concentration (Si_T, based on SiO_2). It should be noted that in this paper, soluble substances are defined as substances that could be detected in samples passed through 0.45-μm filters. They may consist of monomer, ions, oligomers, polymers, and small particles. Analysis of Si_T was carried out through the HF transformation method [38]. Concentrations of Si_a (monomer and dimer silica) and Si_b (oligomer silica) were analyzed by molybdate assay as follows: 40 ml of stock solution of ammonium molybdate was added no more than 5 ml of sample solution in graduated glass tube, then mixing with 2 ml of acetone and 2 ml of oxalic acid, and the total volume diluted to 50 ml with double-deionized water. Spectrophotometry was done at 410 nm, and color-development times were noted [31]. The absorbance recorded at 10 min and the subsequent increase in absorbance from 10 to 30 min were assumed to be due to Si_a and Si_b, respectively. Si_c (polymer silica) could barely react with ammonium molybdate to contribute absorbance within 30 min. The concentration of Si_c was obtained from the difference between Si_T and the sum of Si_a and Si_b. Si_b was not detected throughout treatment of the wastewater probably because of Ostwald ripening that led to the disappearance of particles of intermediate size.

Similarly, the subsamples for analysis of total aluminum were filtered first. Then, filtered sample was digested by the addition of NaOH and boiling as pretreatment. A total of 5.50 ml of ferron solution was transferred into 25 ml graduated glass tube, then mixing with less than 10 ml sample, and diluted to 25 ml with double-deionized water. Spectrophotometry was done at 366 nm, and the total aluminum concentration (Al_T) was calculated using the ultimate absorbance when the monitored absorbance curve reached a plateau [54,55]. This plateau, which is commonly reached within 2 h, was attained when the increase in absorbance was <0.001 per 20 min. Aluminum speciation was carried out through the modified ferron method: Volumes of sample and ferron solution were selected according to the determined Al_T, such that the ferron/total aluminum molar ratio was almost 50. The reaction started upon mixing, and the absorbance was recorded every minute until aforesaid plateau was reached. The absorbance recorded at 1 min and the subsequent increase in absorbance up to the plateau were assumed to be due to Al_a and Al_b, respectively. The Al_c concentration was obtained from the difference between Al_T and the sum of Al_a and Al_b.

To further characterize Al_b, we obtained kinetic constants (*k* values) for the reactions of the various aluminum species with ferron. The absorbance–time function could be fitted with a nonlinear dynamical equation [42]:

$$A_t = a + b\,[1 - \exp(-k_1 t)] + c[1 - \exp(-k_2 t)] \qquad (1)$$

where A_t is the absorbance at time t; a, b, and c are introduction coefficients. Two k values (k_1 and k_2, where $k_1 > k_2$) are constants that, respectively, describe the rates of reaction of ferron reagent with the main polymeric aluminum species that contain the relatively soluble polynuclear species (Al_{b1}) and the relatively insoluble polynuclear species (Al_{b2}). After a, b, k_1, c, and k_2 were obtained, the polymeric aluminum species of Al_b could be identified from its k value.

3. Results and discussion

3.1. Changes in silica species during coagulation with PACl

The traditional process of water treatment by aeration, flotation, coagulation, filtration, and ion exchange has been used for heavy-oil wastewater in Liaohe Oil Field. Specialized techniques for silica removal have not been used. At the reference dosage of PACl for pilot plant treatment (~200 mg/l, based on PACl), the total aluminum concentration was ~1.2 mmol/l. Thus, we studied the coagulation of heavy-oil wastewater by batch experiments using commercial PACl for 2 h. Comparison of characteristics between treated and untreated samples according to common water quality standards showed that pollutants in wastewater precipitated and their concentrations decreased to acceptable levels (Table 1). Levels of silica in water decreased from 473.39 to 230.68 mg/l, although the final level was still well above 50 mg/l. As subsequent filtration and cation exchange have little impact on silica removal, excess silica in boiler water may be a common and serious problem. Thus, it was necessary to study a wide range of PACl dosages for removal of silica.

Fig. 1 shows the effects of commercial PACl on silica removal and the variation of silica species after coagulation for 2 h. The silica concentration decreased from 473.39 to 33.47 mg/l when the PACl dosage increased from 0 to 5 mmol/l (based on aluminum concentration). The Si_T value decreased to 162.35 mg/l when the PACl dosage increased from 0 to 1.5 mmol/l, corresponding to a removal efficiency of 65.7% (removal efficiencies of 51.24 and 71.15% for Si_a and Si_c, respectively). Increasing the dosage to >2 mmol/l appeared to have no significant effect. The Si_T value decreased to 45.57 mg/l at a PACl dosage of 4 mmol/l, corresponding to a removal efficiency of 90.37% (removal efficiencies of 80.96 and 94.12% for Si_a and Si_c, respectively).

The results show that soluble silica and other pollutants could be removed from water using PACl. The silica concentration further decreased to 50 mg/l with the increase in PACl dosage to 4 mmol/l. Evidently, commercial PACl had a greater effect on the removal of Si_c rather than that of Si_a. For example, treatment with a PAC dosage of 4 mmol/l reduced

Table 1
Characteristics of heavy-oil wastewater and standards for feed-water quality

			Water quality standard for heavy-oil wastewater for reuse in steam boilers [1,8]	
Main parameters	Before treatment	After treatment	China	API (USA)
pH	8.39	7.92	7.5–11.0	7.0–12.0
Oil concentration (mg/l)	84.2	1.7	2.0	1.0
Suspended solid concentration (mg/l)	79.4	6.4	2.0	5.0
Silica concentration (mg/l)	473.39	230.68	50.0	150.0
Total iron concentration (mg/l)	0.07	0.02	0.05	0.1
Total alkalinity	1,774.2	972	2,000	2,000
Total hardness (mg/l)	52.1	8.1	0.1	1.0
Total dissolved solids concentration (mg/l)	3,683.6	2,396.4	7,000	7,000

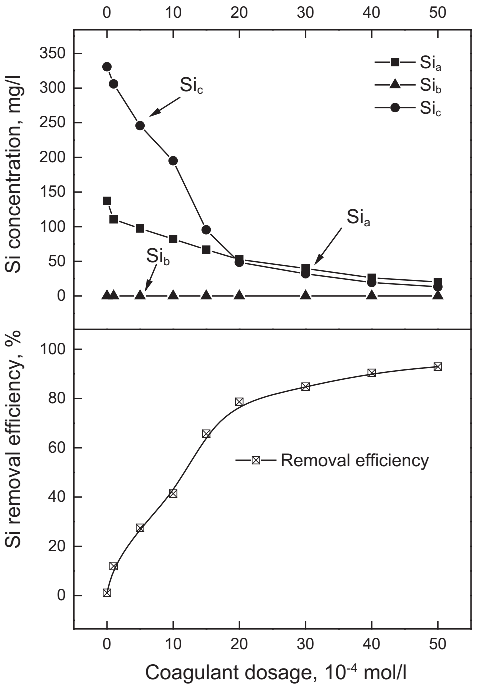

Fig. 1. Effect of commercial PACl on silica removal and variation of silica species.

the proportion of Si_a and Si_c in soluble silicic acid from 29.32 and 70.68% to 57.34 and 42.66%, respectively. Removal depended on the interaction among various species of silica and aluminum hydrolysates in the experiment.

3.2. Variation of silica and aluminum hydrolysates during coagulation

Fig. 2 shows the changes in concentrations of various species of silica and aluminum. These changes occurred during coagulation with 4 mmol/l dosage of commercial PACl within 2 h. The Si_c content dropped sharply within the first 30 min of reaction, slowed down, and then finally stayed at a constant value after 1 h. The Si_a content continuously decreased within 2 h, with the rate of decline slowing down after 30 min. Thus, the rate of decline in Si_c content was larger than that of the decline in Si_a content during the first 60 min. Si_a was the main silica species removed during the last 60 min. Similarly, aluminum speciation varied greatly during different coagulation periods. Concentrations of Al_a and Al_c decreased markedly during the first 30 min and then slowly declined within 2 h. The Al_b content dropped sharply 10 min from the initial time, with the decline decreasing to an efficiency of 60.62% and the rate of decline fluctuating thereafter. The proportion of Al_a to the total aluminum increased and then decreased, while that of Al_b varied in the opposite manner and that of Al_c decreased slowly to a constant value.

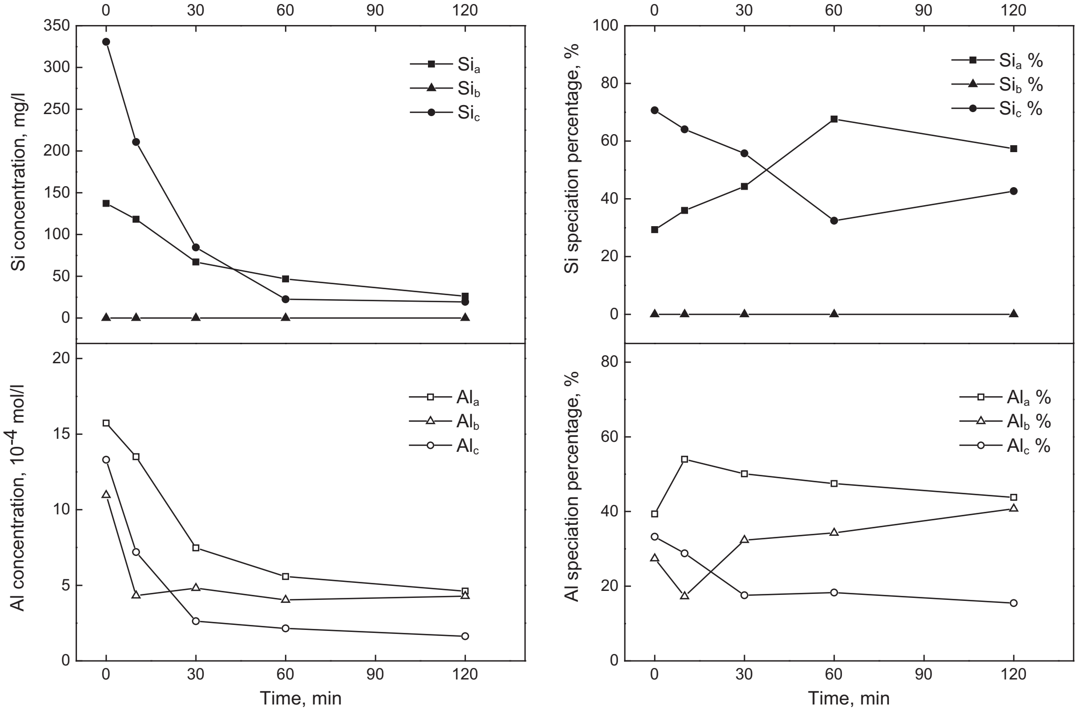

Fig. 2. Variation of silica and aluminum hydrolysates during coagulation with commercial PACl.

Table 2
k values of dynamic parameters for different periods of coagulation with Al_b

t (min)	k_1 (min^{-1})	k_2 (min^{-1})	R^2
0	0.0492	0.0026	0.989
10	0.634	0.0513	0.991
30	0.751	0.0504	0.995
60	0.775	0.0481	0.987
120	0.834	0.834	0.993

Si_c was the major silica species removed within the first 10 min, while the major species of aluminum hydrolysates were those of Al_b and Al_c. Si_a and Si_c concentrations markedly declined during 10 to 30 min when the major species of aluminum hydrolysates were Al_a and Al_c hydrolysates. The rate of decline in Si_a and Si_c concentrations was low for 30–60 min and corresponded with that of Al_a and Al_c at the same time. Within 60 to 120 min, the Si_c content reached equilibrium, while the amounts of Si_a, Al_a, and Al_c continued to decrease slowly. These results imply that removal of Si_a and Si_c mainly depended on their interaction with Al_a and Al_c. The sharp decrease in Al_b content of the water was probably due to rapid adsorption of negatively charged, large, suspended particles. Nevertheless, it was also indispensable to take the complicated interconversion and equilibria of various species of silica and aluminum hydrolysates into consideration. Al_b composition appeared to vary according to the *k* value from the nonlinear simulation equation (Eq. (1)), as shown in Table 2. Values of k_1 and k_2 fluctuate about 0.744, 0.0497, and 0.0026, indicating that there were at least three types of polynuclear species of aluminum formed during 2 h. Relatively insoluble Al_{b2} ($k = 0.0026\ min^{-1}$), which has higher molecular weight [42], disappeared within 10 min. In contrast, the relatively soluble polynuclear species of aluminum ($k = 0.744\ min^{-1}$), which was more soluble than the Al_{b1} ($k = 0.0497\ min^{-1}$), formed with an increasing proportion of Al_b between 10 and 120 min, and finally became the dominant polynuclear species. Preformed Al_b comprised polynuclear species such as Al_{13} and Al_{30} [56], which led to removal of suspended solids. However, Al_b detected after 10 min (higher *k* values) seemed to form *in situ* mainly via self-hydrolysis, which led to a low degree of polymerization and instability compared with the preformed Al_b of PACl.

3.3. Comparison of synthetic PACl samples with various basicities

PACl coagulants with various basicities at identical aluminum concentration were prepared and aged for a week at room temperature before use. Among the prepared samples, PACl products with basicity values of 1.0, 2.2, and 2.5 (denoted as $PACl_{10}$, $PACl_{22}$, and $PACl_{25}$, respectively) were selected, in which Al_a, Al_b, and Al_c were, respectively, dominant. The samples were analyzed and compared (Fig. 3). Concentrations of Al_a, Al_b, and Al_c in $PACl_{10}$ $PACl_{22}$, and $PACl_{25}$ reached 71.24, 70.08, and 67.59%, respectively. PACl samples at a dosage of 4 mmol/l were used with soluble silica for coagulation of heavy-oil wastewater for 2 h.

As shown in Fig. 4, the removal efficiency for major species of silica varied with aluminum speciation of PACl. PACl with higher Al_a content was more efficient at Si_c removal during coagulation. And more efficient removal of Si_a during coagulation was obtained using PACl with higher Al_c content. The Al_b content does not appear to have a correlation with the silica removal data. As mentioned, the Al_b content was more related to coagulation and precipitation of suspended insoluble particles. The detected Al_b after sharp decrease was either excess preformed Al_b of PACl or simple aluminum hydrolysates that were newly formed.

The concentration of PACl species had an significant effect on the removal speed of Si_a and Si_c. Silica concentration declined quickly at first 60 min when the aluminum species were relatively sufficient. However, when the initial active ingredients that refer to both Al_a and Al_c of PACl were expended to a very low value, the speed of silica removal became rather slow. The decline of silica during 60 to 120 min should due to the gradually deposited silica and the newly converted Al_a or Al_c through the transformation of aluminum species. The transformation of aluminum

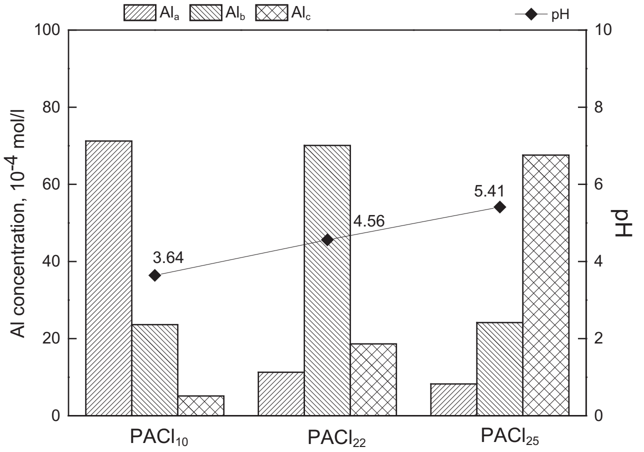

Fig. 3. Aluminum speciation and pH of $PACl_{10}$, $PACl_{22}$, and $PACl_{25}$.

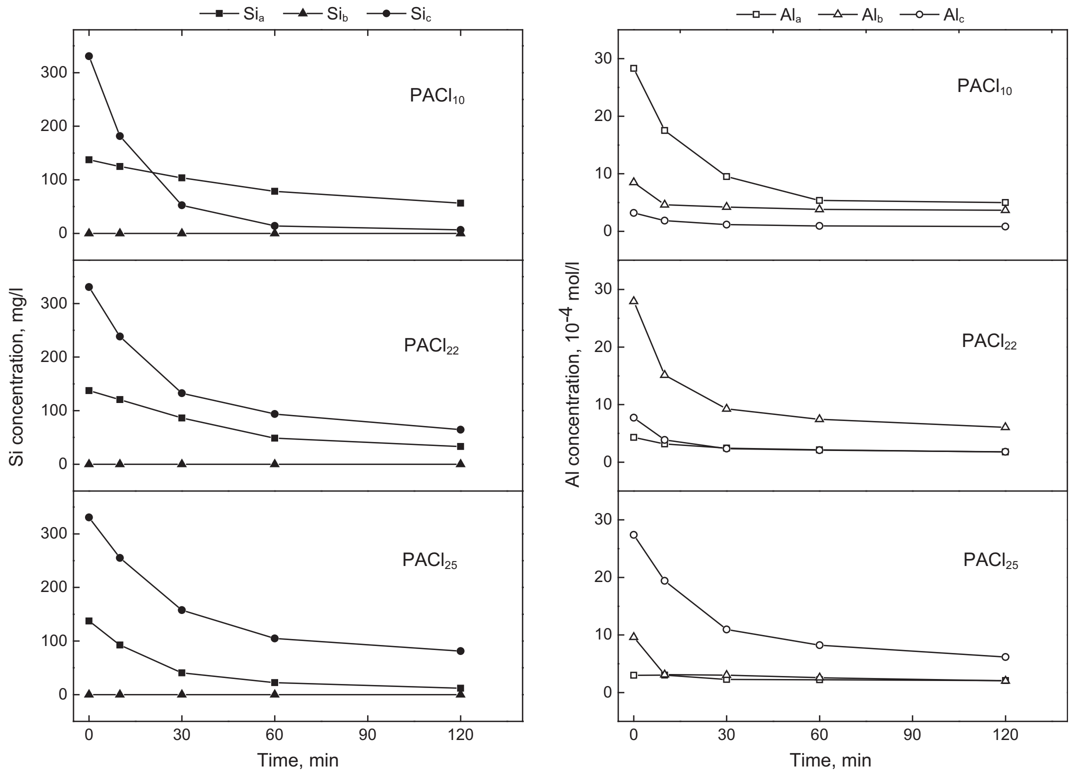

Fig. 4. Variation of silica and aluminum hydrolysates during coagulation with $PACl_{10}$, $PACl_{22}$, and $PACl_{25}$.

species between Al_a, Al_b, and Al_c was more likely to be minor until in the late period during coagulation. During coagulation, the pH value of treated wastewater ranged from 6.78 to 7.42, corresponding to a speciation balance in which neutralized aluminum hydroxide (Al_c) was dominant [57]. But the result showed that Al_c concentrations decreased rapidly regardless of whether or not it was initially dominant. Because the prepolymerized species of PACl are quite stable in a broader pH ranges relative to alum [23]. Besides, the presence of silica would inhibit the normal process of hydrolytic polymerization to form aluminum hydroxide [50,58], thus also weakening the transformation between these aluminum species.

3.4. *Effect of aluminum salts and aluminum hydroxide on silica removal*

Fig. 5 shows the effects of aluminum chloride and of preformed collosol of amorphous aluminum hydroxide on silica removal, as well as the variation of silica and of aluminum hydrolysate concentrations during coagulation with Al_T of 4 mmol/l. As Al_a was the dominant aluminum species when aluminum chloride was combined with wastewater, the Si_c content decreased sharply, while that of Si_a decreased more slowly. Levels of Al_b and Al_c were low throughout the coagulation. Furthermore, the Al_b concentration slightly increased initially probably because of hydrolysis of excess aluminum salts. Al_c was the dominant aluminum species in the collosol of amorphous aluminum hydroxide during the entire treatment. Concentrations of Si_a and Si_c decreased at a relatively moderate rate. During treatment with aluminum chloride, the rate of concentration decrease for Si_a increased rapidly, whereas that of the concentration decrease for Si_c was slight. The amounts of Al_a and Al_b were so low that they were almost undetectable during coagulation with collosol of amorphous aluminum hydroxide.

The effects of Al_a and Al_c in aluminum salt or amorphous aluminum hydroxide on the removal of Si_c and Si_a, respectively, were similar. This similarity is consistent with the above conclusion that the use of aluminum coagulant with high Al_a content and aluminum coagulant with a high Al_c content led to fast and efficient removal of Si_c and of Si_a, respectively. An absorption-modification process can be introduced to explain the mechanism of Si_c removal using Al_a, and the mechanism of Si_a removal using Al_c, based on previous research [43,59–61]. Aluminum ions could absorb on amorphous silica surface and form

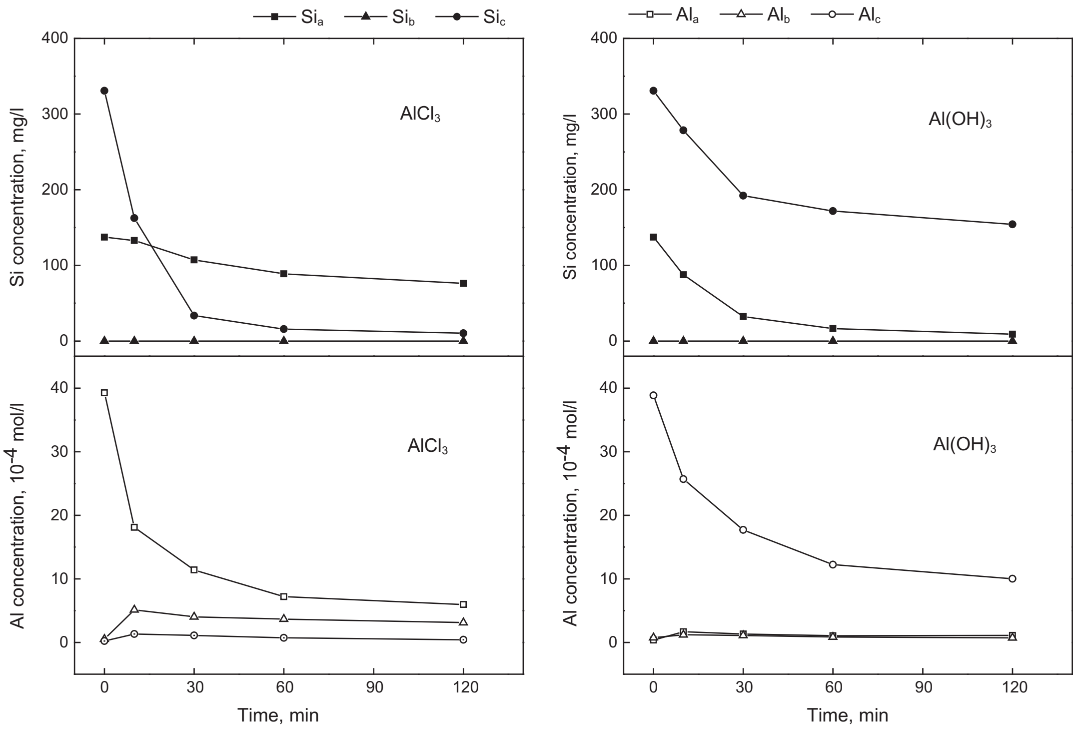

Fig. 5. Variation of silica and aluminum hydrolysate concentrations during coagulation with aluminum chloride and with amorphous aluminum hydroxide.

aluminosilicate sites, consequently preventing the approach of hydroxyl ions, which promotes dissolution of silica [43]. Kuan and Hu [59] proposed the surface precipitation mode to interpret the effect of aluminum salts on the removal of silica, and suggested that the formation of surface precipitate film completely modify the surface properties of silica and protect them against dissolution. The absorbed Al_a likely modified the surface of soluble Si_c, which decreased the solubility and stability [60] of formed admixture, so Si_c could be easily removed from wastewater. Si_a removal together with Al_c was also consistent with the absorption-modification process. Aluminosilicate sites and surface precipitate films resulting from adsorption and deposition [61] of Si_a onto the surface of Al_c decreased the solubility of admixtures with Al_c that were modified by Si_a.

3.5. Discussion

Soluble silica species dispersed in the heavy-oil wastewater varied even when they were in the form of Si_a and Si_c. The range of polymeric silica species (Si_c) varied widely, some of which contained thousands of SiO_2 units and were effectively nanoparticles. The wastewater contained various oils, complex suspended soils, and numerous solutes. Hence, the reaction of silica with aluminum hydrolysates in the environment must be discussed. In this paper, substances in the wastewater are classified into three forms: suspended solids with median particle diameter of >0.45 μm (including most impurities in wastewater and precipitates after coagulation); colloidal particles that are retained in the water passed through 0.45-μm filters (these mainly contain Si_c and Al_c); and soluble monomers, ions, and oligomers, which mostly comprise Si_a and Al_a.

Upon dispersion of PACl in wastewater, preformed aluminum hydrolysates immediately reacted with the all categories of substances in wastewater. Al_b, which is enriched in positive charges, rapidly approached the negatively charged, suspended solids and then formed positively charged patches on the particle surfaces [62]. Electrostatic forces due to interactions between patches on one particle and naked surfaces of other particles caused the particles to aggregate. Meanwhile, the interactions between Al_a and Si_c and between Al_c and Si_a caused soluble silica to become more insoluble and unstable, as mentioned. Admixtures that formed between soluble silica and aluminum hydrolysates gradually approached the primary aggregates with positively charged patches and then led to the growth of large and compact flocs [47], which were essential for sedimentation. During coagulation with continuous reaction and precipitation, soluble silica was progressively removed from the wastewater along with other substances. However, interconversion and equilibria of various species of silica and aluminum hydrolysates were not thoroughly analyzed. These require further studies.

4. Conclusion

PACl had significant effects on the removal of soluble silica through reaction with aluminum hydrolysates. During coagulation of heavy-oil wastewater using PACl at 4 mmol/l, the silica concentration decreased from 473.39 to 45.57 mg/l. Commercial PACl, collosols of amorphous aluminum hydroxide, aluminum salts, as well as PACl synthesized in our laboratory, were used for comparison. The use of PACl with a higher Al_a content and PACl with a higher Al_c content, respectively, led to faster and more efficient removal of Si_c and of Si_a.

An absorption-modification process is proposed to explain Si_c and Si_a modification with Al_a and Al_c, respectively. A coagulation mechanism involving EPC was introduced to explain the reaction of soluble silica and other substances with PACl. The results show the potential of using excess PACl for simple and inexpensive removal of silica and other pollutants. This method may be used to optimize treatment of heavy-oil wastewater.

Acknowledgment

The authors thank the kind help of Jinyu Enterprise Group Corporation of Liaohe Oil Field PanJin for providing water samples.

References

[1] Y. Zeng, C. Yang, W. Pu, X. Zhang, Removal of silica from heavy oil wastewater to be reused in a boiler by combining magnesium and zinc compounds with coagulation, Desalination 216 (2007) 147–159.
[2] F. Luo, B. Dong, J. Xie, S. Jiang, Scaling tendency of boiler feedwater without desiliconization treatment, Desalination 302 (2012) 50–54.
[3] R.Y. Ning, Reactive silica in natural waters—A review, Desalin. Water Treat. 21 (2010) 79–86.
[4] R. Sheikholeslami, I.S. A1-Mutaz, T. Koo, A. Young, Pretreatment and the effect of cations and anions on prevention of silica fouling, Desalination 139 (2001) 83–95.
[5] R. Ganesh, L.Y.C. Leong, R.A. Liske, Evaluation of potential beneficial reuse of San Ardo produced water, Proc. Water Environ. Fed. (2006) 6107–6120.
[6] H. Bill, X. Xie, D. Yan, New technology for heavy oil exploitation wastewater reused as boiler feedwater, Pet. Explor. Dev. 35 (2008) 113–117.
[7] R.J. Jan, T.G. Reed Jr., new caustic process for softening produced water for steam generation, SPE Prod. Eng. 7 (1992) 199–202.
[8] SY/T0097-2000, Design Specification for Heavy Oil Field Produced Water Treatment as Steam Generator Feedwater, Petroleum Industry Publications, Beijing, China, 2001 (in Chinese).
[9] A. Bahadori, H.B. Vuthaluru, Prediction of silica carry-over and solubility in steam of boilers using simple correlation, Appl. Therm. Eng. 30 (2010) 250–253.
[10] K.D. Demadis, E. Mavredaki, A. Stathoulopoulou, E. Neofotistou, C. Mantzaridis, Industrial water systems: Problems, challenges and solutions for the process industries, Desalination 213 (2007) 38–46.
[11] P. Pedenaud, C. Goulay, F. Pottier, O. Garnier, B. Gauthier, Silica scale inhibition for steam generation in OTSG boiler, SPE Prod. Oper. 21 (2006) 26–32.
[12] J. Taler, D. Taler, Tubular type heat flux meter for monitoring internal scale deposits in large steam boilers, Heat Transfer Eng. 28 (2007) 230–239.
[13] B. Hamrouni, M. Dhahbi, Analytical aspects of silica in saline water—application to desalination of brackish waters, Desalination 136 (2001) 225–232.
[14] A.M. Al-Rehaili, Comparative chemical clarification for silica removal from RO groundwater feed, Desalination 159 (2003) 21–31.
[15] R. Sheikholeslami, S. Zhou, Performance of RO membranes in silica bearing waters, Desalination 132 (2000) 337–344.
[16] R. Sheikholeslami, J. Bright, Silica and metals removal by pretreatment to prevent fouling of reverse osmosis membranes, Desalination 143 (2002) 255–267.
[17] F. Mohammadesmaeili, M.K. Badr, M. Abbaszadegan, P. Fox, Byproduct recovery from reclaimed water reverse osmosis concentrate using lime and soda-ash treatment, Water Environ. Res. 82 (2010) 342–350.
[18] H. Roques, Chemical Water Treatment: Principles and Practice, VCH Publications, New York, NY, 1996.
[19] G.M. Ayoub, R.M. Zayyat, M. Al-Hindi, Precipitation softening: A pretreatment process for seawater desalination, Environ. Sci. Pollut. Res. 21 (2014) 2876–2887.
[20] S.A. Thomas, M.E. Yost, S.R. Cathey, Silica removal from steamflood-produced water: South Texas tar sands pilot, SPE Prod. Eng. 2 (1987) 131–136.
[21] L. Dubin, Silica inhibition in cooling water systems, in: C.S. Sikes, A.P. Wheeler (Eds.), Surface Reactive Peptides and Polymers: Discovery and Commercialization, ACS Publications, Washington, DC, 1991, pp. 355–379.
[22] W. Bouguerra, M. Ben Sik Ali, B. Hamrouni, M. Dhahbi, Equilibrium and kinetic studies of adsorption of silica onto activated alumina, Desalination 206 (2007) 141–146.
[23] Y. Matsui, A. Yuasa, Y. Furuya, T. Kamei, Dynamic analysis of coagulation with alum and PACl, J. Am. Water Works Assn. 90 (1998) 96–106.
[24] I.M. Solomentseva, N.G. Gerasimenko, S. Barany, Surface properties and aggregation of basic aluminium chloride hydrolysis products, Colloids Surf., A 151 (1999) 113–126.

[25] Z. Daud, N. Nasir, H. Awang, Treatment of biodiesel wastewater by coagulation and flocculation using polyaluminum chloride, Aust. J. Basic Appl. Sci. 7 (2013) 258–262.

[26] S. Ghafari, H.A. Aziz, M.J.K. Bashir, The use of polyaluminum chloride and alum for the treatment of partially stabilized leachate: A comparative study, Desalination 257 (2010) 110–116.

[27] A. Rabii, G.N. Bidhendi, N. Mehrdadi, Evaluation of lead and COD removal from lead octoate drier effluent by chemical precipitation, coagulation–flocculation, and potassium persulfate oxidation processes, Desalin. Water Treat. 43 (2012) 1–7.

[28] R.Y. Ning, Discussion of silica speciation, fouling control and maximum reduction, Desalination 151 (2003) 67–73.

[29] L.F. Comb, Silica chemistry and reverse osmosis, Ultrapure Water 13 (1996) 41–43.

[30] R.K. Iler, The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica, John Wiley, New York, NY, 1979.

[31] R.K. Iler, Isolation and characterization of particle nuclei during the polymerization of silicic acid to colloidal silica, J. Colloid Interface Sci. 75 (1980) 138–148.

[32] G. Pignalosa, N. Cabrera, A. Mollo, I. Portillo, V. Rouco, L. Vázquez, Silicon determination in Portland cement by fluoride generation, using flame atomic absorption spectrometry, Spectrochim. Acta, Part B 56 (2001) 1995–1999.

[33] J.S. Falcone, J.L. Bass, M. Angelella, E.R. Schenk, K.A. Brensinger, The determination of sodium silicate composition using ATR FT-IR, Ind. Eng. Chem. Res. 49 (2010) 6287–6290.

[34] M.C. Barciela Alonso, R. Prego, Determination of silicate, simultaneously with other nutrients (nitrite, nitrate and phosphate), in river waters by capillary electrophoresis, Anal. Chim. Acta 416 (2000) 21–27.

[35] K. Barla, R. Herino, G. Bomchil, J.C. Pfister, A. Freund, Determination of lattice parameter and elastic properties of porous silicon by X-ray diffraction, J. Cryst. Growth 68 (1984) 727–732.

[36] A.Y. El-Sayed, Y.Z. Hussein, M.A. Mohammed, Simultaneous determination of phosphate and silicate in detergents and waters by first-derivative spectrophotometry, Analyst 126 (2001) 1810–1815.

[37] R. Sheikholeslami, A. Yeung, T. Koo, P.K.R. Yadem, Silica fouling of reverse osmosis membranes-batch and dynamic investigations, in: A.C.T. Barton (Ed.), Chemeca 99: Chemical Engineering: Solutions in a Changing Environment, Institution of Engineers, Newcastle, 1999, pp. 597–604.

[38] R. Sheikholeslami, I.S. Al-Mutaz, S. Tan, S.D. Tan, Some aspects of silica polymerization and fouling and its pretreatment by sodium aluminate, lime and soda ash, Desalination 150 (2002) 85–92.

[39] P.M. Jardine, L.W. Zelazny, Mononuclear and polynuclear aluminum speciation through differential kinetic reaction with ferron, Soil Sci. Soc. Am. J. 50 (1986) 895–900.

[40] D.R. Parker, Identification and quantification of the "Al13" tridecameric aluminum polycation using ferron, Environ. Sci. Technol. 26 (1992) 908–914.

[41] T. Hongxiao, L. Zhaokun, Feature and mechanism for coagulation-flocculation processes of polyaluminum chloride, J. Environ. Sci. 7 (1995) 204–211.

[42] C. Ye, D. Wang, X. Wu, J. Qu, *k*-Value-based ferron assay and its application, J. Colloid Interface Sci. 335 (2009) 44–49.

[43] R.K. Iler, Effect of adsorbed alumina on the solubility of amorphous silica in water, J. Colloid Interface Sci. 43 (1973) 399–408.

[44] B.Y. Gao, H.H. Hahn, E. Hoffmann, Evaluation of aluminum-silicate polymer composite as a coagulant for water treatment, Water Res. 36 (2002) 3573–3581.

[45] N.D. Tzoupanos, A.I. Zouboulis, C.A. Tsoleridis, A systemic study for the characterization of a novel coagulant (polyalminum silicate chloride), Colloids Surf., A 342 (2009) 30–39.

[46] Z. Yang, B. Gao, W. Xu, B. Cao, Q. Yue, Effect of OH^-/Al^{3+} and Si/Al molar ratios on the coagulation performance and residual Al speciation during surface water treatment with poly-aluminum-silicate-chloride (PASiC), J. Hazard. Mater. 189 (2011) 203–210.

[47] W. Xu, B. Gao, Y. Wang, Q. Zhang, Q. Yue, Influences of polysilicic acid in Al_{13} species on floc properties and membrane fouling in coagulation/ultrafiltration hybrid process, Chem. Eng. J. 181–182 (2012) 407–415.

[48] Z. Yang, B. Liu, B. Gao, Y. Wang, Q. Yue, Effect of Al species in polyaluminum silicate chloride (PASiC) on its coagulation performance in humic acid-kaolin synthetic water, Sep. Purif. Technol. 111 (2013) 119–124.

[49] P.D. Taylor, R. Jugdaohsingh, J.J. Powell, Soluble silica with high affinity for aluminum under physiological and natural conditions, J. Am. Chem. Soc. 119 (1997) 8852–8856.

[50] W. Wang, H. Yang, X. Wang, J. Jiang, W. Zhu, Factors effecting aluminum speciation in drinking water by laboratory research, J. Environ. Sci. 22 (2010) 47–55.

[51] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.

[52] S.K. Dentel, Application of the precipitation-charge neutralization model of coagulation, Environ. Sci. Technol. 22 (1988) 825–832.

[53] D. Wang, H. Tang, J. Gregory, Relative importance of charge neutralization and precipitation on coagulation of kaolin with PACl: Effect of sulfate ion, Environ. Sci. Technol. 36 (2002) 1815–1820.

[54] C. Changui, W.E.E. Stone, L. Vielvoye, J.M. Dereppe, Characterization by nuclear magnetic resonance spectroscopy, ferron assay, and acidification of partially neutralized aluminium solutions, J. Chem. Soc., Dalton Trans. (1990) 1723–1726.

[55] G.L. Kerven, P.L. Larsen, F.P.C. Blamey, Detrimental Sulfate Effects on Formation of Al-13 Tridecameric Polycation in Synthetic Soil Solutions, Soil Sci. Soc. Am. J. 59 (1995) 765–771.

[56] Z. Chen, C. Liu, Z. Luan, Z. Zhang, Y. Li, Z. Jia, Effect of total aluminum concentration on the formation and transformation of nanosized Al_{13} and Al_{30} in hydrolytic polymeric aluminum aqueous solutions, Chin. Sci. Bull. 50 (2005) 2010–2015.

[57] Y.H. Choi, J.A. Nason, J.H. Kweon, Effects of aluminum hydrolysis products and natural organic

matter on nanofiltration fouling with PACl coagulation pretreatment, Sep. Purif. Technol. 120 (2013) 78–85.
[58] J. Duan, J. Gregory, The influence of silicic acid on aluminium hydroxide precipitation and flocculation by aluminium salts, J. Inorg. Biochem. 69 (1998) 193–201.
[59] W.H. Kuan, C.Y. Hu, Chemical evidences for the optimal coagulant dosage and pH adjustment of silica removal from chemical mechanical polishing (CMP) wastewater, Colloids Surf., A 342 (2009) 1–7.
[60] R.K. Iler, The effect of surface aluminosilicate ions on the properties of colloidal silica, J. Colloid Interface Sci. 55 (1976) 25–34.
[61] F.J. Hingston, M. Raupach, The reaction between monosilicic acid and aluminium hydroxide. I. Kinetics of adsorption of silicic acid by aluminium hydroxide, Aust. J. Soil Res. 5 (1967) 295–309.
[62] C. Ye, D. Wang, B. Shi, J. Yu, J. Qu, M. Edwards, H. Tang, Alkalinity effect of coagulation with polyaluminum chlorides: Role of electrostatic patch, Colloids Surf., A 294 (2007) 163–173.