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The Effect of Polymer Flocculant Used for Basic Oxygen Furnace (BoF) Scrubbing Water Treatment on the Thixotropic Behaviour of Conditioned Sludge

HSIN-HUNG OU*, CHIUNG-HSUN LIN, HSIN-HSIUNG CHEN** and YU-BIN HONG*****

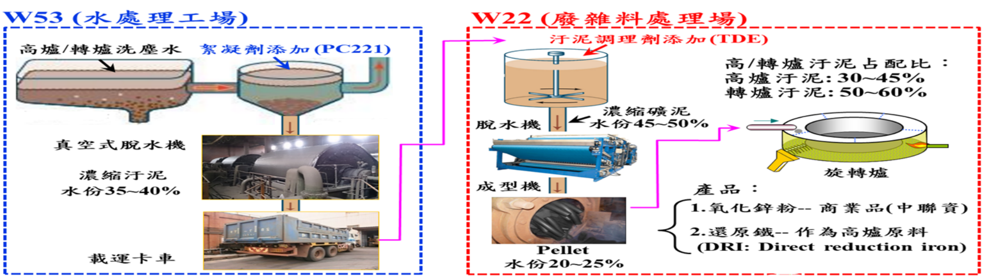
** New Materials Research & Development Department*
***Utilities Department*
****Ironmaking Department*
China Steel Corporation

This study examines the effect of the cationic flocculant used for BoF scrubbing water treatment and its performance as a sludge conditioner for the valuable product recovery from flocculated sludge. Regarding the scrubbing water treatment, either flocculation or the dewatering performance of BoF dust slurry was less dependent on the ion strength of the flocculant solution, as the effect of compression of the electrical double layer could be neutralized by a sufficient flocculation retention time. However, the sludge flocculated by flocculant with relatively high ion strength failed to meet the requirement of thixotropic behaviour in the downstream recovery process. This process failure was owing to a build-up of rebuilding energy of conditioned sludge, which was likely resulting from a relatively low degree of polymer chain extension. On site examination also revealed that the feature of flocculant used in the upstream scrubbing water treatment significantly affected the thixotropic characterization of conditioned sludge, determining the performance of filter medium in the downstream recycling process. In the case of the highly chain extended flocculant used in the scrubbing water treatment, the lifetime of filter clothes in the downstream recycling process has been raised to the regular level (i.e. 700~800 hrs) along with an enhanced treatment capacity of sludge (i.e.11,000~13,000 tons per month).

Keywords: Flocculation, Sludge conditioner, Thixotropic behaviour

1. INTRODUCTION

Accounting for 74% of the world's total output of crude steel, the steelmaking by blast furnace (BF)/ basic oxygen furnace (BoF) process is a dominant steelmaking technology. For cleaning of BF/BoF exhaust gas, the wet scrubber facility is essential and complementary to the BF/BoF process, as large quantities of dust in the BF/BoF exhaust gas can be efficiently removed. The removal of dust from the scrubbing water turns to a required process for water recycling, and is mostly conducted by a flocculation process with cationic polyacrylamide. As long as the suspended dust is flocculated into a sludge, the recycling of precious products from flocculated BF/BoF sludge is economically meaningful, as BF/BoF dust is a mixture of iron oxides along with other element oxides in lesser amounts. In making achievements in the circular economy, China Steel Corporation (CSC) has attempted to recycle reduced iron powder and zinc oxide from BF/ BoF sludge by the rotary hearth furnace (RHF) process for the last ten years. During the precious metal recycling process, the flocculated BF/BoF sludge gathered from the scrubbing water treatment plant is subject to sludge conditioning by anionic polyacrylamide (sludge conditioner), dewatering and extrusion process prior to the RHF process. The overall recycling process of precious metals within BF/BoF dust in CSC is shown in Scheme 1.



Scheme 1 An overall recycling process of precious products from BoF/BF dust in CSC.

In CSC, the treatment capacity of BF/BoF sludge by RHF process is in the range of 12,000~15,000 tons per month and the monthly produced amount of major product (i.e. zinc oxide) is around 6,500 tons. However, during the period from May 2016 to Mar. 2017, the treatment capacity of BF/BoF sludge was reduced by 20~60% because the lifetime of filter clothes was down to 300~400 hrs (regular lifetime of filter clothes is in the range of 700~800 hrs). The poor performance of filter cloth was confirmed to be responsible for the reduced treatment capacity of BF/BoF sludge. In fact, the performance of filter clothes is likely dependent on the rheological characterization of conditioned sludge which is significantly determined by the feature of flocculant used in the scrubbing water treatment. Several studies have investigated the effect of solid content, temperature and on the rheology characterization of sewage sludge. For example, Baroutian et al. (2013) concluded that the shear stress of a mixture of primary and secondary sewage increases with an increase in solid content, which is owing to the presence of superficial grouping including proteins and polysaccharides. In another study, Chen et al. (2005, 2006) indicated that the bare wastewater sludge mostly showed typical viscoelastic liquid-like behaviour whereas the polymer-flocculated sludge behaviours as a solid-like material. On the other hand, Mikkelsen et al. (2001) also indicated that the shear sensitivity of the sludge is associated with the resistance to filtration and the degree of dispersion in response to the turbulent shear.

Although there have been lots of studies examining the relationship between rheological characterization of sludge and the parameters of the process in which sludge operates, however, so far, it appears that no study attempts to investigate how the flocculant feature for BF/BoF scrubbing water treatment affect the thixotropic behaviour of conditioned sludge during the recycling process. This study aims to investigate the effect of flocculant features on the thixotropic characterization of conditioned sludge. Practical field testing was also conducted to examine the effect of upstream flocculant for scrubbing water treatment on the downstream treatment capacity of conditioned sludge.

2. MATERIALS & METHODS

2.1 Flocculation of BoF scrubbing water

BoF scrubbing water samples were taken from the scrubbing water treatment plant, which were then stored at 4^0C after sampling. The pH of the BoF scrubbing water fell to around 8.1 ± 0.2 with a concentration of suspended solids of 300~450ppm. Two proprietary flocculants indexed as flocculant A and B were examined for the kinetics of dust flocculation and their dewatering performance. Both flocculant A and B were composed of cationic polyacrylamide and sodium sulphate while the portion of sodium sulphate in flocculant B was less than that of flocculant A. A 1000ppm of the stock flocculant solution was prepared with ultra-pure water which was stored for use no longer than 2 weeks. A jar test was conducted on a six-place gang at 60^{o}C with the optimal flocculant dosage of 1ppm (1ml of stock flocculant solution was added into 1L of the scrubbing water). The scrubbing water sample was subjected to no pH adjustment prior to the jar test. After the dosage, the solution was rapidly mixed at 120 rpm for 3min, followed by a slower mixing speed of 30rpm for another 10min. The flocculated dust (flocculated sludge) was gathered after leaving the slurry solution standing for a further 10min. The entire contents in the beakers were filtered and carefully gathered by pouring the flocculated sludge into a Buchner funnel for filtration at 0.015 MPa vacuum pressure. This process took 5~6 min until the vacuum reading no longer changed. The flocculated sludge in the presence of flocculant A and B were indexed as flocculated sludge A and B, respectively. The water content of obtained flocculated sludge was also measured by calculating the difference of sludge weight before and after drying treatment at 105^{o}C.

2.2 Thixotropic experiment of flocculant and conditioned sludge

5g of flocculated sludge was subsequently conditioned with a desired amount of anionic polyacrylamide (TDE), which was indexed as conditioned sludge A and B, respectively. The obtained conditioned sludge A and B were stored in Ziplock bags for less than 3 days before examining the thixotropic behaviour of the conditioned sludge. A parallel plate rheometer (AR-G2, TA instrument) was used to determine the thixotropic feature of the conditioned sludge. The sludge sample was subjected to pre-shear at 50s^{-1} for 10s, in order that different samples all acquire the same degree of internal structure before rheological measurement. After the pre-shear process, the sludge was dealt with a short period of rest (30s) and then a successive increasing (0 to 3000s^{-1} in 3min) and decreasing (3000 to 0s^{-1} in 3min) shear rates. The experiments were carried out at room temperature (25~27^{0}C). On the other hand, a rheological behaviour of proprietary flocculant was also conducted. 3ml of the 1ppm flocculant liquid was placed within the annulus of rotational cylinders by the same rheology procedure as above (i.e. each rheology test consisted of a pre-shear, rest period, and thixotropic test). An energy dispersive X-ray analyser (EDX) was also used to provide the elemental identification and quantitative compositional information of the retired filter clothes. The particle size distribution of BF/BoF slurry was also determined by the particle size analyser.

3. RESULTS AND DISCUSSION

3.1 Rheology behaviour and particle size distribution of BF/BoF dust slurry

Regarding the RHF process in CSC, BF and BoF flocculated sludge is integrated into a single stream prior to the RHF recycling process. In order to clarify which sludge could adversely affect the performance of the filter cloth, a preliminary examination on the rheological behaviour of BF/BoF dust slurry (BF/BoF dust in the scrubbing water) was conducted, as shown in Fig.1. The BF dust slurry follows one of the typical rheology behaviour of non-Newtonian fluid, i.e. it gives a clear yield point and shows shearing thinning behaviour. However, in the case of BoF dust slurry, some abrupt changes were found in the viscosity during the shearing process. This result accounts for the complex structure of BoF dust. In addition to the totally different rheogram pattern, Fig.1 also reveals that the yield point of BF dust slurry is far smaller than that of BoF dust slurry. In fact, the yield point is associated to the transformation of sludge from viscoelastic to plastic phase which is responsible for the formation of a fractal interconnected network. This result about the yield point possibly implies that BF slurry is rather compressible as compared to BoF slurry.

As a practical matter, the above results may be indicative of a strong induced force being exerted from the conditioned BoF sludge to the filter medium during the dewatering process of conditioned sludge. The dewatering filter medium, while dealing with only conditioned BoF sludge, likely suffers from the damage and so performs badly. Therefore, a designated weight ratio between flocculated BF and BoF sludge was prepared and conditioned prior to the RHF process in CSC. Instead of conditioned BF sludge, this study only investigated conditioned BoF sludge in terms of the effect of polymer type and dosage on the thixotropic feature of conditioned BoF sludge, as the feature of conditioned BoF sludge principally determine the performance of the dewatering filter cloth during the recycling process.

3.2 Performance of flocculant for scrubbing water treatment (BF/BoF dust slurry)

With either flocculant A or B, the flocculation performance of BF dust slurry is better than that of BoF dust slurry, which is likely as a result of the diversity of particle size distribution (Fig.2). No significant difference on the settling kinetics of floc was observed, indicating that the diversity of particle size distribution of BF slurry appears to compensate for the effect of electrical double layer contributed by the flocculate feature on the flocculation performance. This result is likely owing to the fact that the agglomeration of dust particles in the BF slurry

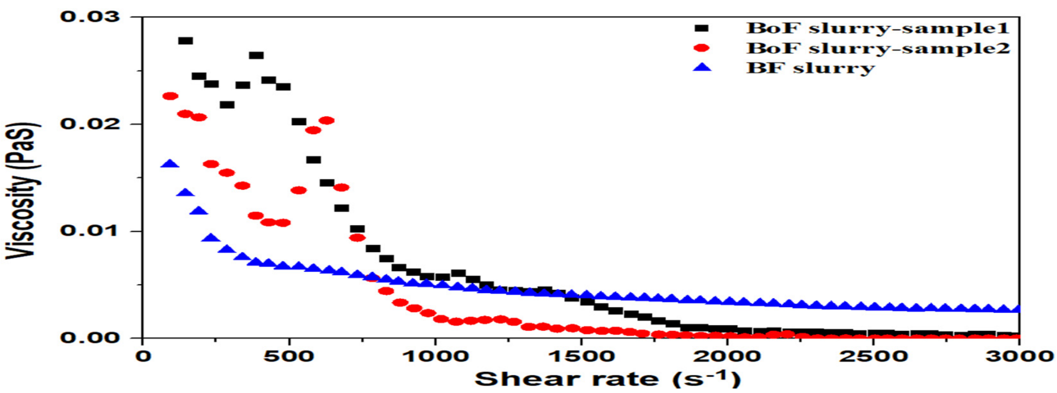


Fig.1. Rheological characterizations of BF and BoF slurry.

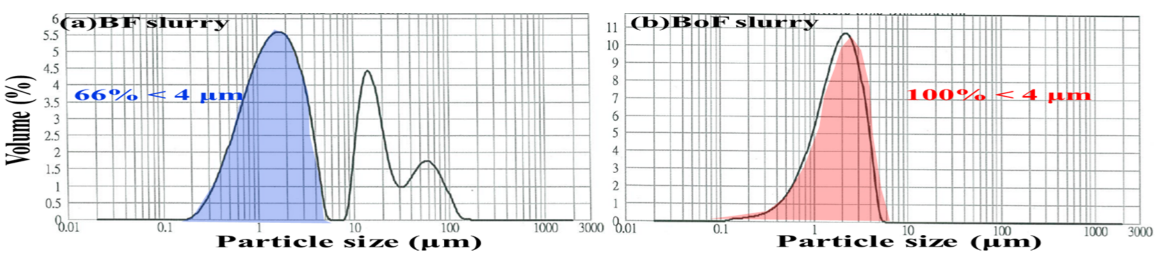


Fig.2. Particle size distribution of (a) BF slurry and (b) BoF slurry.

was mainly dominated by the bridging flocculation mechanism rather than compression of the electric double layer.

In the case of BoF slurry, the performance difference between flocculant A and B was obvious. Either flocculation kinetics or floc dewatering performance made by flocculant A was found to be better than that of flocculant B (Data not shown). This result indicates that the effect of flocculant feature on the BoF dust flocculation could not be neutralized by the uniform particle size distribution of BoF dust. In other words, the flocculation of BoF dust is dominated by the compression of the electrical double layer and flocculate B with a relatively high amount of Na_2SO_4 is in favour of the BoF dust flocculation. Furthermore, a difference on the zeta potential of BoF dust after the addition of either flocculation A or B was observed, which further confirmed that the charge neutralization on the dust surface induced by the adsorbed polymer was mainly responsible for the BoF dust flocculation.

3.3 Thixotropic feature of conditioned BoF sludge

Figure 3 shows the thixotropic behaviour of conditioned sludge A and B, both of which show that the decreasing rheogram is lower than the increasing rheogram. This result reveals the dissipation of rebuilding energy of sludge after the shearing process. Also, no abrupt stoppage of rheogram plot for either sludge A or sludge B was observed, indicating no viscosity bifurcation of the sludge (i.e. the conditioned sludge belongs to liquid-like material even at a relatively low shear rate). Presumably the solid concentration within the sludge is at a similar level (from the same scrubbing water sample), the difference in the thixotropic curve between sludge A and B could be as a result of the flocculant feature.

On the other hand, the value of the hysteresis area can be considered as a measure of the degree of thixotropy (Battisttoni 1997). The enclosed area of the hysteresis loop in the case of sludge A (Fig.3a~c) is far smaller than the case of sludge B (Fig.3f~g), indicating no obvious thixotropic breakdown of sludge A structure. In contrast, sludge B is subject to the consumption of rebuilding energy during the structure breakdown and rebuilding. Furthermore, the enclosed area of the hysteresis loop in the case of sludge B appears to increase with increasing flocculant dosage. This result shows that the rebuilding energy of sludge B owing to an overdose of flocculant B in the treatment of scrubbing water could be dissipated completely. No build-up of rebuilding energy is indicative of a more thixotropic structure of sludge B than that of sludge A. In fact, the rheological behaviour of sludge is dependent on the competition between colloidal forces which tend to rebuild the structure (i.e. physical aging) and hydrodynamic forces which tend to break the solid structure (i.e. shear rejuvenation) (Baudez 2008). In the case of sludge A, colloidal forces are dominant which keep the structure intake and result in an elastic sludge. Comparatively, sludge B mainly undergoes hydrodynamic influence whereby the network structure weakens.

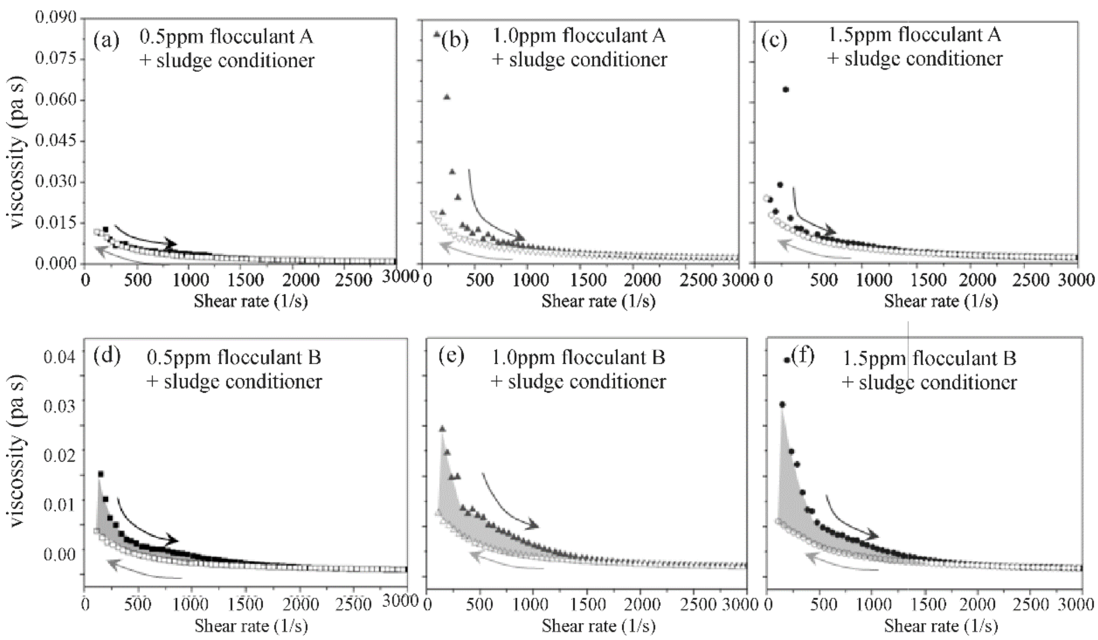


Fig.3. Thixotropic behaviour of conditioned sludge A (a~c) and B (e~g) as a function of flocculant dosage.

The viscosity of sludge A by the end of the backward shear curve increases with an increase in flocculant dosage whereas that of sludge B seems to be irrespective of the flocculant dosage. This result further confirmed that the structure network of sludge A is more incompressible than sludge B. The photographies of conditioned sludge after thixotropic experiments (sludge breakdown and rebuilding process) are shown in Fig.4. Sludge A after thixotropic experiment appears to be elastic and with a higher dosage of flocculant could result in being more elastic. Sludge A is also able to stretch and be returned to its original shape and size, however, sludge B seems more viscos than sludge A. This phenomenon corresponds to the aforementioned result that the rebuilding energy of sludge B could be dissipated more. From a practical point of view, during the dewatering process, the remaining rebuilding energy within sludge B could lead to a relatively low shear force to filter media, allowing for a low impact (long service time) on filter cloths.

3.4 Effect of the flocculant feature on the thixotropic feature of conditioned sludge

Since the flocculant polymers are supplied in a solid form for reasons of economy, ease of transportation and storage. Each particle is presumably a hard packed tangle of long polymer chains similar to a ball of string. Therefore, the conformation (degree of chain extension) of flocculant polymer in the solution played a very important role in the flocculation system and even for the sludge rheology (Yu & Somasundaran 1996). For example, the ion strength of flocculant solution was reported to determine the extension degree of the polymer chain. The surface of negatively charged dust particles may not find enough space to accommodate all incomplete chain extended flocculant before the flocculant-dust complex could reach isoelectric point. An incomplete extended polymer could therefore provide a possible inter-attractive force to affect the rheological characterization of sludge. It was therefore expected that the rigid sludge structure could be found in cases where the polymer was coiled and twisted.

Based on the thixotropic test of flocculant solution (Fig.5), flocculant B rather shows a typical non-Newtonian fluid feature, as compared to flocculant A. In addition, the rheogram of flocculant A is higher than that of flocculant B. This result may imply that, before complete extension of flocculant polymer, the polymer chain of flocculant B is believed to gradually extend with no interference, whereas the polymer chain of flocculant A may partly extend into the solution to give loops and tails, giving a random twisted and coiled configuration with much smaller dimensions until complete extension. The repulsion between charged groups within flocculant A could be “screened” by SO_4^{2-} in the solution, in much the same way that the effect of double-layer repulsion is reduced at high salt concentrations. Comparatively, flocculate B may present a significant repulsion between segments of the polymer chain and hence a typical extension from the typical random coil configuration.

On the other hand, it appears that flocculant A is completely destroyed after $1670s^{-1}$, while in the case of flocculant B it takes place after $1350s^{-1}$. The inference

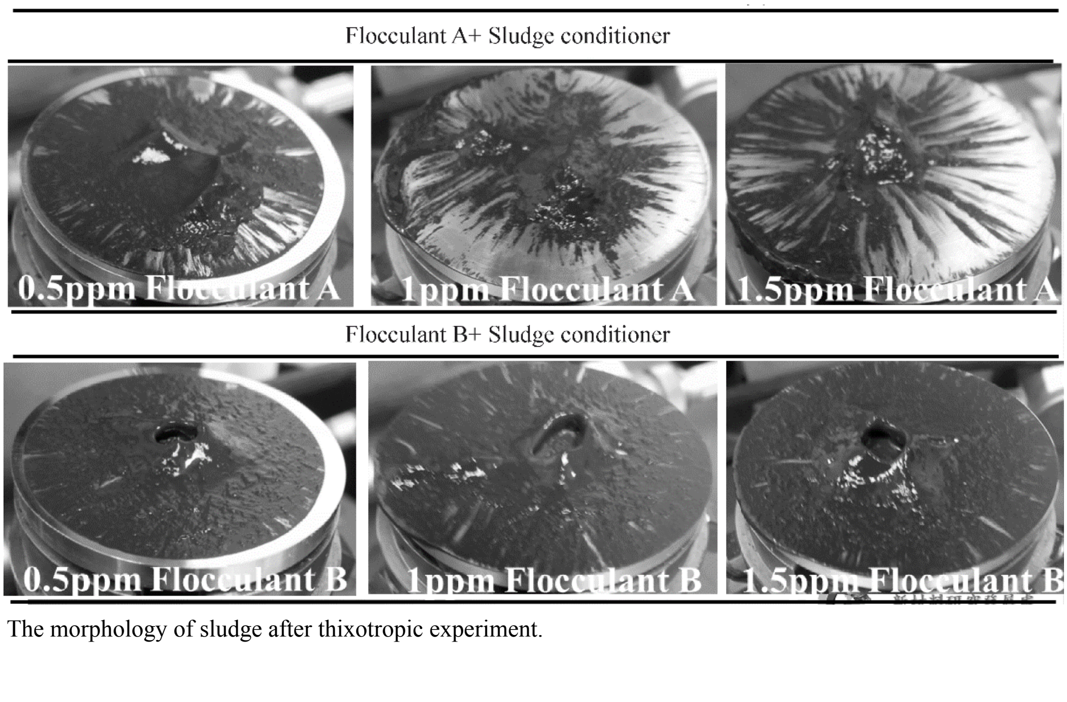


Fig.4. The morphology of sludge after thixotropic experiment.

could be confirmed because the forward and back rheogram curves present a very similar pattern after the above shear rates, and the second forward and backward rheogram hysteresis curves are closely overlapped with the result of the water sample (following Newtonian fluid feature). In other words, the effect of ionic strength of polymer solution does affect the extension of the polymer chain before polymer collapse. The difference is exhibited due to the presence of a different Na_2SO_4 amount, resulting in more SO_4^{2-} ions in the flocculant A solution than that of the flocculant B solution. In fact, the self-extension of the polymer A chain owing to the repulsive force between the positively charged function group units would be neutralized by SO_4^{2-}. This result may lead to an adverse effect on the polymer chain extension, resulting in an unexpected flocculant conformation. Therefore, a relatively high shear rate is required to achieve the complete chain extension of flocculant A and even for polymer collapse. The uncoiled and twisted flocculant A is more likely to create the build-up of cations and become an adsorption core of TDE anionic polymer. This result is possibly again against the extension of the sludge conditioner. For this reason, ionic strength has an important effect on the polymer chain extension in aqueous solutions, and leading to the change in the rheological characterization of conditioned sludge.

3.5 On-site investigation on the performance of the recycling process

As mentioned previously, the flocculant is purchased as a solid form and a simple mixer is required on site to dissolve the flocculant with a fixed agitation power. Without considering the complete extension of flocculant polymer, the effect of flocculant characterization on the rheological characterization of sludge likely determines the performance of filter medium in the recycling plant. In terms of the treatment performance of BoF scrubbing water by either flocculation A or B, the water qualities in the presence of both flocculates meet the effluent regulation (i.e. suspension solid < 60 ppm, T-Fe < 2ppm, and the water content of sludge is in the range of 48~52wt%). There has been no negative response from the field engineers in the scrubbing water treatment plant in using either flocculant A or B. This result is corresponding to the laboratory conclusion that, as long as the retention time is enough, the removal efficiency of suspended solid is less dependent on the flocculate feature.

However, the recycling performance of conditioned sludge A showed a totally different result from that of conditioned sludge B. In the case of conditioned sludge B, the service lifetime of the filter cloth used in the dewatering process was between 800~920hr which was nearly a 2.7-fold increase compared to that of sludge A. The processing capacity and recycling yield in the case of sludge B were also enhanced by 2.6 and 1.7 times, respectively, as compared to that of sludge A. The on-site testing result also corresponds to the laboratory conclusion that the conditioned sludge A is relatively incompressible and subsequently the shearing action on the filter medium limited the performance of the cloth filter medium. Further investigation on the retired filter clothes by SEM when dealing with conditioned sludge A and B are demonstrated in Fig.6a & 6b. The filter mesh in the case of conditioned sludge A seems to be clogged by a sticky material (containing N and Cl elements as confirmed by EDX analysis, which are also major elements of cationic polyacrylamide), while the filter media for treating sludge B is surrounded and enclosed by iron oxide particles. The on-site evidence from SEM investigation confirmed the formation of random coiled flocculant A as a result of the presence of an overdose of Na_2SO_4. The unclear SEM image of the filter cloth in the case of sludge A is further evidence of the existence of remaining flocculanton in the filter medium, because of the accumulation and build-up of static electric charges which takes place on the non-conducting specimen surface during SEM analysis.

SEM results provide solid evidence about the fact that the improved service life of filter cloth together with the enhanced processing capacity and yield of recycling product is as a result of the preferential viscous feature

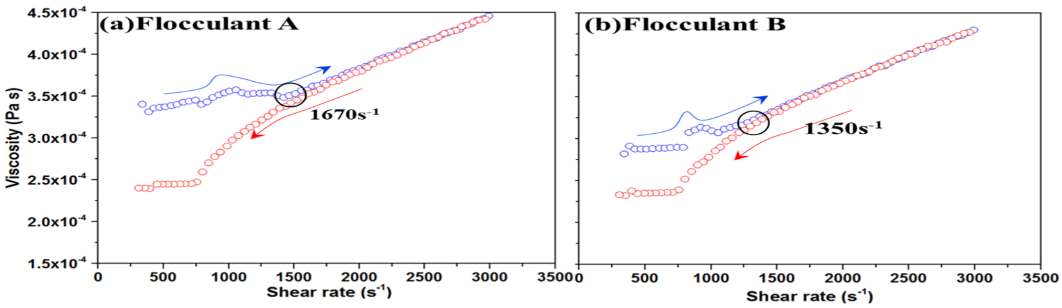


Fig.5. Rheological characterization of flocculant A(a) and B(b).

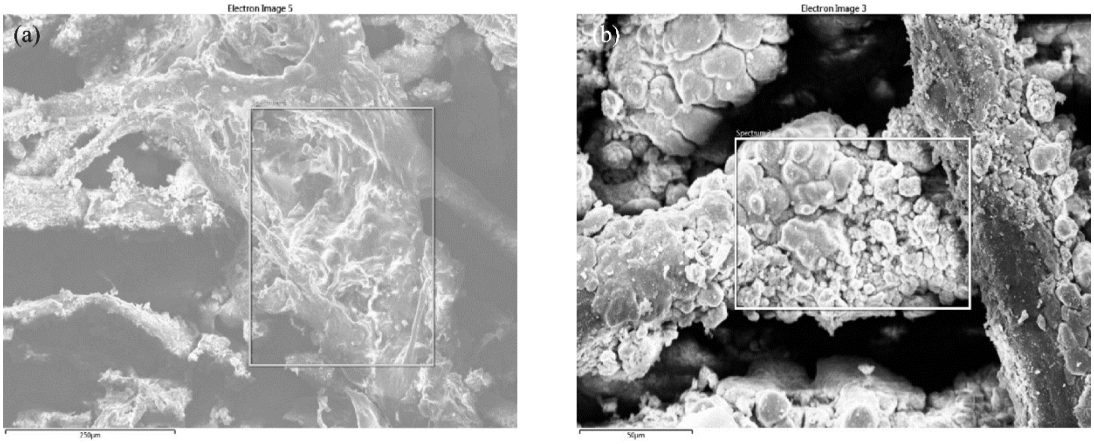


Fig.6. SEM image of retired filter cloth after treating sludge A(a) and B(b).

of sludge B. In other words, the performance of the downstream recycling process of conditioned sludge is significantly dependent on the characterization of flocculant used in the upstream water treatment process. The poor performance of filter clothes is owing to the induced shear force on the filter medium during the sludge dewatering process, which is likely to be observed by the thixotropic behaviour of conditioned sludge.

4. CONCLUSIONS

This study aims to investigate the impact of the flocculant feature on the performance of the recycling process of precious metal from the conditioned sludge. A thixotropic analysis on flocculation solution accounts for the flocculant conformation being determined by the ion strength owing to the presence of Na_2SO_4. Despite the flocculation performance of BoF dust is irrespective of the flocculant conformation, the rheological characterization of conditioned sludge is likely dependent on the flocculation conformation. This is because an inappropriate conformation of flocculant may lead to a build-up of rebuilding energy within the sludge during the shearing process. In terms of the practical recycling process of precious products from conditioned sludge, the conformation of flocculant is mainly responsible for the poor performance of filter clothes, as an unexpected thixotropic degree of sludge may induce a shear force on the filter medium. In the case of the highly chain extended flocculant used in the upstream scrubbing water treatment, the lifetime of filter clothes in the downstream recycling process has been raised to a regular level (i.e. 700~800 hrs) along with an enhanced treatment capacity of sludge (i.e.11,000~ 13,000 tons per month).

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