

煤化工浓盐水对煤泥水沉降特性的影响

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摘要:煤化工浓盐水中含有大量无机盐离子,外排污染环境,且处理和回收成本较高。由于煤化工浓盐水含有的无机盐离子与选煤常用凝聚剂有效离子成分类似,本文以煤化工浓盐水作为煤泥水处理的凝聚剂,以内蒙古某地区难沉降不黏煤为研究对象,研究了浓盐水用量对煤泥水沉降特性的影响。采用多重散射光分析仪对煤泥水系统稳定性进行分析,通过激光粒度分析仪分析了煤泥颗粒粒度变化,以聚丙烯酰胺作为絮凝剂,研究了浓盐水用量对煤泥水沉降和澄清液浊度的影响。结果表明,结晶盐用量0~62.5 kg/t,未添加浓盐水时,煤泥水系统比较稳定,动力学稳定性指数(TSI)无明显变化;随着结晶盐用量增加,煤泥颗粒开始凝聚,TSI值显著增加,结晶盐用量为50 kg/t时,煤泥水顶部TSI达到最大值,此后TSI值随结晶盐用量的增加开始减小。同时,煤泥表面Zeta电位随着结晶盐用量增加先迅速升高后趋于稳定,表明结晶盐中的阳离子具有压缩双电层,降低表面电位的作用。粒度分析结果表明,未添加浓盐水时,煤泥水颗粒 D_{50} 为9.43 μm, D_{90} 为45.57 μm;结晶盐用量为12.5 kg/t时,煤泥水颗粒 D_{50} 增加至11.92 μm, D_{90} 增加至63.77 μm,说明浓盐水的加入促进了颗粒凝聚。煤泥水沉降试验结果与TSI变化规律基本一致,随着结晶盐用量的增加,煤泥沉降速度逐渐加快,结晶盐用量为50 kg/t时,沉降速率达到最大值,上层澄清液浊度达到最小值。试验结果表明,煤化工浓盐水可有效促进煤泥颗粒之间的凝聚,提高难沉降煤泥水的沉降效果。可考虑将煤化工浓盐水作为煤泥水处理凝聚剂引入煤泥水处理系统中,以降低浓盐水处理成本,提高煤泥水处理效果,但浓盐水对于整个选煤工艺系统分选指标、产品性能和设备寿命等方面的影响仍需进一步研究。

关键词:浓盐水;多重散射光分析仪;煤泥水;沉降特性;凝聚

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Effect of saline wastewater of coal chemical industry on the sedimentation characteristics of coal slurry

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Abstract: The saline wastewater of coal chemical industry contains a large amount of inorganic salt ions. For saline wastewater, the discharge will cause environmental pollution, while the treatment and recovery cost is relatively high. In this paper, saline wastewater of coal chemical industry was used as a coagulant for coal slurry as the inorganic salt ions in the saline wastewater were similar to the effective ionic components of the coagulant. The influence of saline dosage on the sedimentation characteristics of coal slurry was discussed with non-stick coal sample from Inner Mongolia. The stability of coal slurry was analyzed by a turbiscan lab. The changes of the coal particle size were measured by a laser particle size analyzer. The effects of saline dosage on the sedimentation effect and supernatant turbidity were studied with polyacrylamide as a flocculant. The results show that the coal slurry system is relatively stable when no saline wastewater is added and the turbiscan ability index (TSI) has no obvious change. With the increase of saline dosage at 0~62.5 kg/t, the coal particles begin to agglomerate, and the TSI value increases significantly. The TSI at the top area of the coal slurry reaches a maximum value when saline dosage is 50.0 kg/t, then the TSI value begins to decrease when saline dosage is further added. Simultaneously,

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the zeta potential of the coal slime surface increases rapidly and then tends to be steady with the increase of saline dosage, indicating that the cations in the saline have an effect on compressing electric double layer and reducing the surface potential. The results of particle size analysis show that the D_{50} and D_{90} of the coal slime particles is 9.43 μm and 45.57 μm separately without adding saline wastewater. And these two values increase to 11.92 μm and 63.77 μm , separately, when 12.5 kg/t saline dosage is added, demonstrating that the addition of saline wastewater promotes the coagulation among particles. The results of slurry water sedimentation test are basically consistent with TSI, and the settling rate of the coal slurry gradually accelerates with the increase of saline dosage. When the saline dosage is 50 kg/t, the settling rate reaches the maximum value and the supernatant turbidity reaches the minimum value. The results show that the saline wastewater can effectively promote the coagulation of coal slime particles and improve the sedimentation effect of difficult-to-settle slurry water. Therefore, saline wastewater from coal chemical industry can be considered to use as a coagulant for coal slurry in order to reduce the treatment cost of saline wastewater and improve the sedimentation effect of coal slurry. However, the influences of saline wastewater on the separation index, product performance and equipment life in the whole coal preparation process system need further study.

Key words: saline wastewater; turbiscan lab; coal slurry; sedimentation characteristics; coagulation

0 引言

面对日益增长的社会需求,我国煤多、油少、气贫的资源赋存状况为煤化工行业提供了良好的发展前景^[1-2]。煤化工废水的处理是煤化工发展过程中需解决的一个关键问题,煤化工废水实现“零排放”需要经过物化预处理、生化处理、深度处理以及浓盐水蒸发结晶4个过程^[3]。经深度处理后,大约有70%的煤化工废水进入循环系统,而未回收的废水则成为浓盐水。浓盐水水质复杂,含盐量大,种类多,如钠盐、钙盐、镁盐、硝酸盐、硅酸盐、磷酸盐和氯化物等,并含有一定量的有机物,不能直接排放,容易危害周边生态环境^[4-5]。目前,膜分离处理技术是浓盐水处理中最常用的方法,与传统浓缩工艺相比,具有技术成熟、能耗低、操作简单等特点^[3,6-8],但膜表面容易被污染,膜通道容易被浓盐水中的悬浮物和结垢离子堵塞,清洗困难^[9-10]。经过膜浓缩后,仍剩余大约10%左右的浓缩液,此溶液称为高浓盐水^[11],目前常采用蒸发技术处理。根据蒸发动源主要由自然和非自然蒸发2种。由于自然蒸发速度慢,存在一定的环境风险,因此煤化工浓盐水自然蒸发存在一定争议^[12]。非自然蒸发有机械蒸发和多效蒸发^[8]等,蒸发效率较高,但非自然蒸发的设备费用和能耗均有所增加^[4]。

煤化工高浓盐水中存在大量 Na^+ 、 Ca^{2+} 、 Mg^{2+} 等金属阳离子^[11,13],与选煤用凝聚剂有效离子成分类似,可考虑作为凝聚剂,用于选煤厂煤泥水处理,因此高浓盐水的资源化利用备受关注。荣用巧等^[14]研究发现煤制甲醇厂的浓盐水含有大量无机阳离子,可替代常规的无机凝聚剂,提高煤泥水沉降效果,结果表明煤泥水沉降可降低浓盐水总硬度和碱度,降低浓盐水中 Ca^{2+} 、 Mg^{2+} 含量。熊亮

等^[15]研究表明煤化工浓盐水对难沉降煤泥水的自由沉降具有促进作用,并发现浓盐水盐度对煤泥水沉降效果有一定影响,盐度过高,煤泥水沉降效果变差。虽然目前已有部分研究表明煤化工浓盐水可用于改善选煤厂煤泥沉降效果,但浓盐水作用下的煤泥水沉降特性和作用机理比较复杂,浓盐水作用下颗粒的表面性质和煤泥沉降特性有待进一步研究。本文以内蒙古某选煤厂难沉降煤泥水为研究对象,通过采用多重散射光稳定性分析仪,研究了煤化工浓盐水用量对煤泥水系统稳定性和沉降特性的影响,并对煤泥水沉降过程中的颗粒粒度变化进行分析,研究不同浓盐水用量对颗粒表面Zeta电位的影响。

1 试验

1.1 试验样品

1.1.1 浓盐水样品

浓盐水样品采自内蒙古某化工厂,为便于定量分析浓盐水中结晶盐的用量,将浓盐水进行蒸发得到结晶盐,然后加入去离子水,配成溶解性总固体含量为50 g/L的浓盐水溶液。采用离子色谱对制备得到的浓盐水进行离子含量分析,水质分析结果见表1。浓盐水 $\text{pH}=9.26$,呈碱性,总硬度为34.40 mmol/L。溶液中主要阳离子为 Na^+ ,浓度为 $19.854 \cdot 10^{-6}$,其次为 Mg^{2+} ,浓度为 $100.64 \cdot 10^{-6}$, K^+ 和 Ca^{2+} 含量相对较少;主要阴离子为 Cl^- ,浓度为 $22.652.97 \cdot 10^{-6}$,其次为 SO_4^{2-} ,浓度为 $2.413.32 \cdot 10^{-6}$, NO_3^- 和 PO_4^{3-} 含量相对较少。

1.1.2 煤泥水样品

煤泥水样品取自内蒙古鄂尔多斯某选煤厂,为加药前的一段尾煤浓缩机入料,煤种为不黏煤。煤泥水样品经过滤、低温干燥后,密封储存备用。

表1 浓盐水水质分析

Table 1 Quality analysis of saline wastewater

指标	数值
pH	9.26
总碱度/(mg·L ⁻¹)	237.51
总硬度/(mmol·L ⁻¹)	34.40
色度/PCU	1 243
浊度/NTU	0
电导率/(μm·cm ⁻¹)	86 200
Cl ⁻ 含量/10 ⁻⁶	22 652.97
SO ₄ ²⁻ 含量/10 ⁻⁶	2 413.32
NO ₃ ⁻ 含量/10 ⁻⁶	186.71
PO ₄ ³⁻ 含量/10 ⁻⁶	21.4
Na ⁺ 含量/10 ⁻⁶	19 854.10
K ⁺ 含量/10 ⁻⁶	26.04
Ca ²⁺ 含量/10 ⁻⁶	8.55
Mg ²⁺ 含量/10 ⁻⁶	100.64

采用BT-9300Z激光粒度仪对煤泥的粒度组成进行分析,结果如图1所示,煤泥平均粒度为17.21 μm,D₅₀=9.44 μm,粒度分析结果表明煤泥中含有大量<10 μm的微细颗粒,大量微细颗粒的存在会对煤泥水沉降产生一定影响。

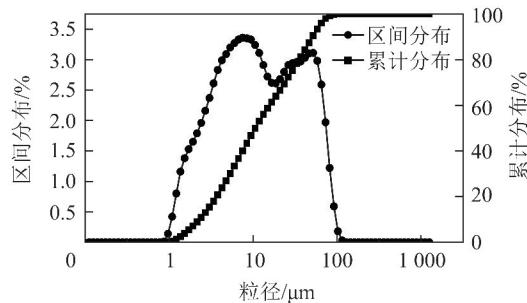


图1 煤泥颗粒的粒度分布

Fig. 1 Particle size distribution of coal slime sample

通过X射线衍射分析仪对煤泥的矿物组成进行分析,结果如图2所示,煤泥中主要黏土矿物为高岭石和石英,还含有少量长石、伊利石和方解石等。高岭石遇水易泥化,使煤泥水中的细泥含量显著增加。黏土矿物表面一般呈电负性,颗粒间相互排斥,不易产生凝聚,导致煤泥沉降困难^[16-20]。

1.2 试验方法

1.2.1 样品稳定性分析

多重散射光稳定性分析仪(Turbiscan lab)通过透射光或背散射光的光通量反映样品某一截面浓度随时间的变化^[21-23],从而定量分析样品的动力学稳定性指数(TSI)。TSI值越大,样品稳定性越差,越易产生沉降。TSI计算公式为

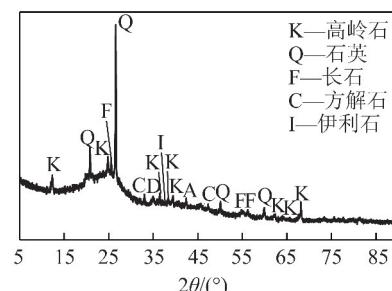


图2 煤泥X射线衍射图

Fig. 2 X-ray diffraction diagram of coal slime

$$TSI = \sum_{i=1}^n \frac{\sum h | scan_i(h) - scan_{i-1}(h) |}{H} \quad (1)$$

式中,H为样品总高度;h为扫描点高度;scan_i(h)和scan_{i-1}(h)分别为扫描点高度为h时,第i次和第i-1次扫描获得的光强度值^[24-25]。

每次配制浓度40 g/L的煤泥水溶液100 mL。将不同体积的浓盐水溶液与煤泥水混合均匀后,取出20 mL置于一个高度55 mm、容积30 mL的测量瓶中,采用多重散射光稳定性分析仪进行测量。

1.2.2 絮凝沉降试验

每次配制浓度为40 g/L的煤泥水450 mL,将其置于500 mL的具塞量筒中,加入不同体积的浓盐水,上下晃动10次后,再加入用量12.5 g/t的聚丙烯酰胺,上下晃动10次,开始记录澄清层厚度随沉降时间的变化,并绘制煤泥水沉降曲线。同时,沉降8 min后,取上层清液通过浊度计(WGZ-800),测量其浊度值。

1.2.3 Zeta电位测试

采用电位分析仪(Malvern Zetasizer Nano ZS90)测试煤泥表面Zeta电位。配制浓度为40 g/L的煤泥水溶液450 mL,与不同体积的浓盐水溶液混合均匀并沉降24 h,移取5 mL液面以下5.0 mm处的溶液作为测试样品,每组样品测试3次,取平均值。

1.2.4 粒度分析

采用激光粒度分析仪(BT-9300Z)测量不同结晶盐用量下煤泥颗粒的粒度分布。样品的制备过程与稳定性分析试验制备步骤基本一致,取与不同体积浓盐水混合后的煤泥水样品,采用激光粒度分析仪在无超声分散的条件下进行测试,每组试验测试3次,取平均值。

2 试验结果与分析

2.1 结晶盐用量对TSI值的影响

为更好地分析煤泥水稳定性的变化情况,将测试区域分成底部(0~8 mm)、中部(8~34 mm)

和顶部(34~41 mm)3部分。结晶盐用量对TSI值的影响如图3所示。随沉降时间的延长,煤泥水TSI值整体呈上升趋势。煤泥水TSI值随结晶盐用量的增加而增加,50 kg/t时,TSI达到最大值,此后进一步增加结晶盐用量,TSI值开始降低。TSI值随煤泥颗粒浓度的变化而变化,TSI值越大

表明煤泥水系统越不稳定,煤泥越容易沉降。当结晶盐用量为62.5 kg/t时,煤泥水TSI值略有下降,可能是由于煤泥水中金属阳离子过量造成。煤泥水系统顶部TSI值的变化最大,主要是添加浓盐水后,煤泥水系统极不稳定,煤泥发生沉降,顶部最先出现澄清层。

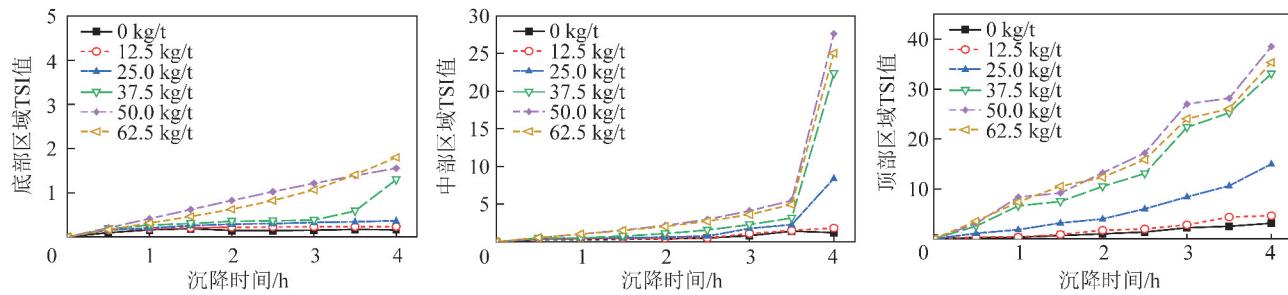


图3 结晶盐用量对煤泥水系统TSI值的影响

Fig. 3 Effect of saline dosage on TSI value of coal slurry

2.2 结晶盐用量对Zeta电位的影响

结晶盐用量对煤泥颗粒表面Zeta电位的影响如图4所示。随着结晶盐用量增加,煤泥颗粒表面Zeta电位迅速提高,结晶盐中的金属阳离子在结晶盐用量超过50 kg/t时,煤泥表面Zeta电位逐渐趋于稳定。研究表明金属阳离子具有压缩双电层,降低表面电位,促进煤泥颗粒凝聚的作用。廖祥磊等^[26]研究表明金属阳离子达到一定浓度时,颗粒表面吸附处于饱和状态,表面电位趋于稳定。

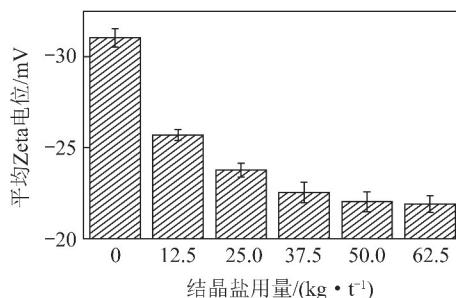


图4 结晶盐用量对煤泥表面Zeta电位的影响

Fig. 4 Effect of saline dosage on Zeta potential of coal slime surface

2.3 结晶盐用量对煤泥颗粒粒度分布的影响

结晶盐用量对煤泥颗粒粒度分布的影响如图5所示。随着结晶盐用量的增加,煤泥颗粒粒度整体呈先增加后趋于平稳的趋势。未添加浓盐水的时候,煤泥水颗粒 D_{50} 为9.43 μm, D_{90} 为45.57 μm;结晶盐用量为12.5 kg/t时,煤泥水颗粒的 D_{50} 增加至11.92 μm, D_{90} 增加至63.77 μm;随着结晶盐用量的增加,煤泥颗粒粒度呈增加趋势,至结晶盐用量增加至50 kg/t后,煤泥颗粒粒度略有减小,说明浓盐水的加入使煤泥水颗粒产生了比较明显的凝聚作用。

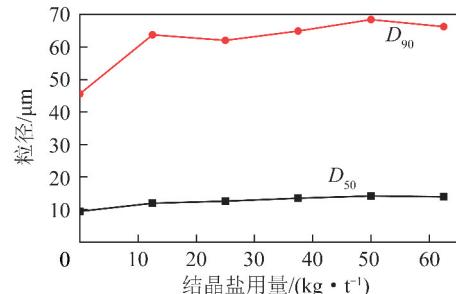


图5 结晶盐用量对煤泥水粒度分布的影响

Fig. 5 Effect of saline dosage on particle size distribution of coal slurry

2.4 结晶盐用量对煤泥水沉降效果的影响

结晶盐用量对煤泥水沉降效果的影响如图6所示。在相同的絮凝剂用量下,未添加浓盐水时,煤泥颗粒沉降速度缓慢;随着结晶盐用量的增加,煤泥颗粒沉降速度先增加后略有减小;结晶盐用量超过50 kg/t后,其沉降速度下降。煤泥颗粒沉降速度变化规律与煤泥水系统TSI值的变化规律基本一致。表明浓盐水对煤泥水沉降具有较好的凝聚作用。

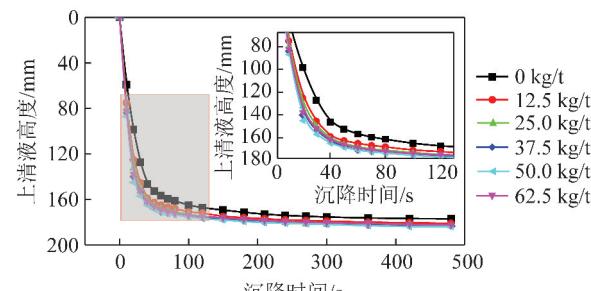


图6 结晶盐用量对煤泥水沉降效果的影响

Fig. 6 Effect of saline dosage on sedimentation effect of coal slurry

在煤泥水沉降曲线中,通过计算各沉降曲线沉降段的斜率,可得到不同结晶盐用量下煤泥颗粒的沉降速度,结果如图7所示。可知浓盐水的加入显著提高了煤泥水的沉降速度。当煤泥水系统中未加入浓盐水时,沉降速度为4.23 mm/s,结晶盐用量为50 kg/t时,沉降速度增至7.25 mm/s。

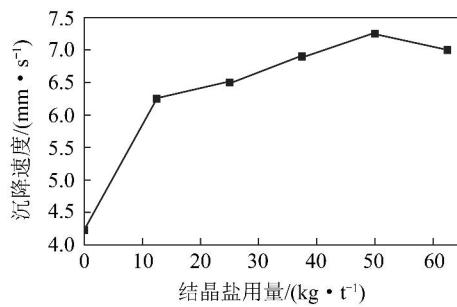


图7 结晶盐用量对煤泥水沉降速度的影响

Fig. 7 Effect of saline dosage on sedimentation velocity of coal slurry

2.5 结晶盐用量对煤泥水上清液浊度的影响

为进一步验证结晶盐作为凝聚剂处理难沉降煤泥水的效果,对不同结晶盐用量下,煤泥水澄清后的上清液浊度进行分析,结果如图8所示。未添加浓盐水时,其上清液浊度达到324 NTU;结晶盐用量增加到50 kg/t时,其浊度达到最小值,为173 NTU;此后随结晶盐用量加大而略有升高。表明结晶盐用量超过一定范围后,颗粒间的凝聚作用有下降趋势,加入适量浓盐水,浓盐水中阳离子在带负电的黏土颗粒表面吸附,会降低颗粒表面负电位,促进颗粒之间的凝聚,但溶液中阳离子超过一定浓度后,会在颗粒表面形成饱和或多层吸附,反而会降低颗粒的凝聚效果^[27]。

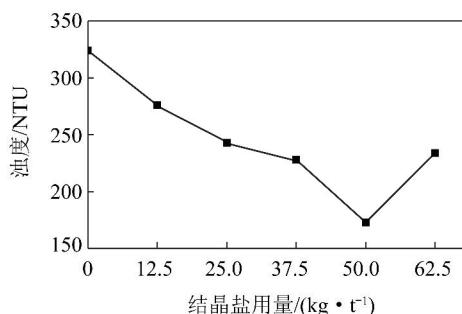


图8 结晶盐用量对煤泥水上清液浊度的影响

Fig. 8 Effect of saline dosage on supernatant turbidity of coal slurry

3 结论

1) 浓盐水溶液中主要阳离子为 Na^+ ,其浓度为 $19.854 \cdot 10^{-6}$, 主要阴离子为 Cl^- , 其浓度

为 $22.652.97 \cdot 10^{-6}$,其余离子含量相对较少。煤泥水样品中含有大量 $<10 \mu\text{m}$ 微细颗粒,主要的黏土矿物为高岭石,会对煤泥水沉降产生一定影响。

2) 煤泥水中未添加浓盐水时,TSI值变化很小,煤泥水系统稳定,未发生明显的煤泥沉降现象。加入浓盐水后,TSI值逐渐增大,在浓盐水结晶盐用量为50 kg/t时,TSI达到最大值。TSI值的增大说明结晶盐的加入使煤泥水系统失稳,煤泥水系统出现了比较明显的沉降现象。

3) 结晶盐用量小于50 kg/t时,煤泥颗粒表面Zeta电位随着结晶盐用量的增加迅速升高,说明结晶盐中的阳离子具有压缩双电层,降低表面电位的作用。结晶盐用量进一步增加,煤泥表面Zeta电位趋于稳定。同时,随着结晶盐用量的增加,煤泥颗粒粒度呈增加的趋势,结晶盐用量大于50 kg/t后,煤泥颗粒粒度略有减小,说明浓盐水的加入使煤泥颗粒产生了比较明显的凝聚作用。

4) 在相同的聚丙烯酰胺用量下,结晶盐用量为50 kg/t时,煤泥的沉降速度达到最大值,上清液浊度达到最小值。表明浓盐水对难沉降细粒煤泥的沉降效果具有明显的促进作用。

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