

草浆原料的湿法除氯和钾元素试验研究

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摘要:为了解决草浆黑液在流化床中燃烧时易烧结的问题,采用湿法预处理的方式来减少黑液中氯和钾元素的含量。分别选择 25 ~ 100 °C 的去离子水以及 25 °C 的 0.25 mol/L 的氢氧化钠和柠檬酸溶液来对稻秆和麦秆进行浸泡试验,使用液-质联用色谱仪(LC-MS)以及原子发射光谱仪(ICP-OES)对浸泡液中氯和钾离子的浓度进行测量,并通过扫描电镜得到在不同条件下浸泡后的稻秆和麦秆的表面微观结构,得出了浸泡时间、浸泡温度以及酸和碱对生物质中氯和钾元素浸出的影响。结果表明:浸泡温度的增加能够破坏生物质细胞壁,从而促进稻秆和麦秆中氯和钾元素的浸出。0.25 mol/L 的氢氧化钠溶液几乎不会影响稻秆和麦秆中氯和钾元素的浸出。0.25 mol/L 的柠檬酸溶液会抑制麦秆中氯离子的浸出,对稻秆中氯离子的浸出则几乎没有影响。此外,0.25 mol/L 的柠檬酸溶液还能有效地提高稻秆和麦秆中钾元素的浸出率。水浸法除氯和钾元素的效果很好,在 100 °C 下浸泡 3 h 后,氯和钾元素的浸出率分别超过 95.18% 和 85.12%。

关键词:湿法预处理;氯和钾元素;浸出率;柠檬酸;氢氧化钠

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引言

黑液是造纸碱法煮浆段所产生的废液,是造纸业 COD 高排放的主要来源^[1-2],其主要成分为木质素、纤维素、半纤维素、碳水化合物和无机化合物^[3]。根据造纸原料的不同,黑液一般可以分为木浆黑液和草浆黑液。目前,有较多种的黑液处理方式,例如氧化法、生物处理法、物理化学法以及碱回收法^[4-9]。其中,碱回收法可以在处理黑液的同时回收黑液燃烧所产生的能量和碱,这使它成为最经济有效的黑液处理方法。目前,木浆黑液已经可以在传统碱回收炉内稳定燃烧并实现热量和碱的回收,但是在使用传统碱回收技术处理粘度更高且热

值较低的草浆黑液时,出现了给料困难、需要添加辅助燃料以及蒸发器堵塞等问题^[10-11]。近年来,流化床碱回收技术被提出来解决草浆黑液的处理问题^[12],该技术具有燃料适应性好、热效率高、投资低以及 NO_x 和 SO₂ 排放低等优点^[13],但是,在草浆黑液的流化床燃烧过程中,经常会出现床料烧结的问题,这会极大地影响流化床的正常运行,该问题也成为使用流化床碱回收法来处理草浆黑液的最大障碍。

草浆黑液中氯和钾元素含量较木浆黑液高很多,且相关的研究已经指出这两种元素的存在是造成床料烧结的主要原因^[14-16]。氯和钾元素会在燃烧过程中与碱金属元素反应生成熔点很低的碱金属共熔体,随后这些低熔点共熔体会在高温下熔融成为粘性流体并覆盖在床料表面从而造成床料的烧结。因此,如何减少黑液中氯和钾元素的含量是解决床料烧结问题的关键。由于在燃烧过程中氯和钾元素很难被去除,因此预处理成为降低黑液中氯和钾元素含量的最佳方式。草浆黑液中的氯和钾元素全部来自于煮浆所用的草类原料中,所以去除草料中的氯和钾元素也就降低了其在黑液中的含量。有研究表明,生物质中的氯和钾大部分都是以游离态的或是具有离子交换性的形式存在的^[17-19],所以本文考虑采用浸泡的方式来减少生物质中的氯和钾元素含量。本试验以稻秆和麦秆为原料,分别研究了浸泡时间、浸泡温度以及酸碱溶液对氯和钾元素浸出效果的影响。该研究可为草浆黑液流化床碱回收技术的应用奠定基础。

1 试验部分

1.1 试验材料

试验所用稻秆和麦秆均产自于安徽阜阳,两种

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生物质中氯和钾元素的含量如表 1 所示。其中氯元素为 X 射线荧光光谱分析(XRF)所得,钾元素则是将生物质使用高氯酸、浓硝酸和 30% 双氧水消解后通过原子发射光谱分析(ICP-OES)所得。

表 1 稻秆和麦秆中氯和钾元素的含量

Tab. 1 Cl and K contents of rice and wheat straw

| 元素含量 wt/% | 稻秆 | 麦秆 |
|-----------|------|------|
| K | 2.10 | 2.30 |
| Cl | 0.76 | 1.17 |

在酸碱浸泡试验中,酸和碱分别选择为柠檬酸和氢氧化钠。选择柠檬酸的主要原因为:若使用硫酸和硝酸作为浸泡液,黑液中会存在 SO_4^{2-} 和 NO_3^- , 这两种酸根离子会和碱金属元素反应生成低熔点共熔体从而促进床料的烧结。若使用盐酸则会引入氯离子从而影响试验结果的测量。为了避免以上问题的出现,选择有机酸中酸性较强的柠檬酸作为酸性浸泡液。试验所用的氢氧化钠和柠檬酸溶液的浓度均为 0.25 mol/L。

1.2 试验装置与分析仪器

试验所使用的浸泡液加热及恒温装置为 HH-8 型恒温水浴锅,该设备的控温精度为 $\pm 1^\circ\text{C}$ 。生物质浸泡液中的氯离子和钾离子浓度分别采用液-质联用色谱仪(LC-MS,ICS-3000,美国戴安)和全谱直读电感耦合等离子体原子发射光谱仪(ICP-OES,Optima 5300DV,美国珀金埃尔默)来测量。在不同条件下浸泡后的稻秆和麦秆的微观形貌由扫描电镜(Quanta 200F,美国 FEI)来观测。

1.3 试验步骤

本试验共分两组,第一组用于研究不同温度的去离子水对于生物质中氯和钾元素浸出的影响;第二组则用于研究酸碱溶液对于生物质中氯和钾元素浸出的影响。试验前先将稻秆和麦秆切碎分段,每段长度约 10 mm,随后将切碎的稻秆和麦秆置于 105°C 的干燥箱内干燥 2 h。取 4 g 干燥后的麦秆和稻秆分别放入 500 mL 的烧杯中。在第一组试验中,分别向烧杯中加入 250 mL 已预热至设定温度(25、50、75 和 100°C)的去离子水,随后将烧杯置于对应温度下的水浴锅中以保持恒温,浸泡时间分别选取为 0.5、1、2 和 3 h。在第二组试验中,分别向烧杯中加入 25°C 的 0.25 mol/L 的氢氧化钠溶液和柠檬酸溶液,随后将烧杯置于 25°C 的水浴锅内以保持恒

温,浸泡时间为 3 h。两组试验进行时,均使用塑料薄膜盖住烧杯口以最大限度的减少浸泡液的蒸发量。在达到设定浸泡时间后,从水浴锅内取出烧杯并将生物质从浸泡液中滤出,对生物质进行电镜扫描以获取不同条件下浸泡后的微观形貌。同时,测量浸泡液中氯离子和钾离子的浓度并测量剩余浸泡液体积,随后通过公式(1)计算出麦秆和稻秆中氯和钾元素的浸出率。

浸出率(%) =

$$\frac{\text{浸泡液体积(L)} \times \text{浸泡液中离子浓度(g/L)}}{\text{生物质质量(g)} \times \text{生物质中对应元素含量(\%)}} \times 100\% \quad (1)$$

2 结果与讨论

2.1 温度对氯和钾元素的浸出效果影响

2.1.1 温度对氯元素浸出效果的影响

稻秆和麦秆中氯元素浸出率随温度以及时间的变化规律如图 1 所示。

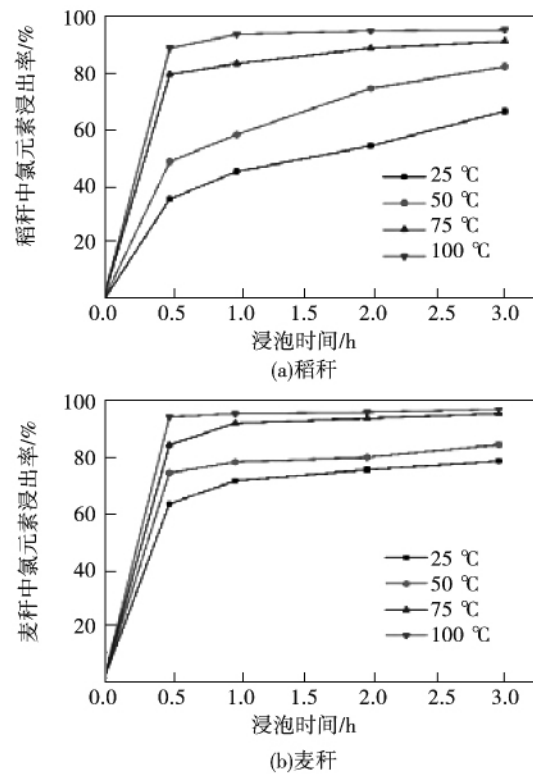


图 1 不同温度下稻秆和麦秆中氯元素浸出率变化

Fig. 1 Changes in leaching rate of Cl in rice and wheat straw at different temperatures

由图可知,稻秆和麦秆中氯元素的浸出规律相似。在前半小时内,氯元素浸出速度最快,且其浸出速度随着温度的升高而增加。特别是当温度高于 75 °C 以后,浸出速度的增加较为明显。浸泡超过半小时后,所有温度下氯元素的浸出速度均明显降低。100 °C 时,浸泡 2 h 后的麦秆和稻秆中氯元素的浸出率已几乎不再变化,这说明此时两种生物质中的可溶性氯元素已几乎完全被浸出。在所有温度下,麦秆中氯元素的浸出率均高于相同浸泡时间下的稻秆,由此可以得知水浸法对于麦秆中氯元素的去除效果更好。稻秆在 25、50、75 和 100 °C 下浸泡 3 h 后的氯元素浸出率分别为 66.72%、82.34%、91.14% 和 95.18%,相对应的麦秆中氯元素浸出率分别为 77.91%、83.70%、94.65% 和 96.29%。根据以上数据可知,温度的提高能够有效促进生物质中氯元素的浸出,但当温度升高至 100 °C 后的浸出效果较 75 °C 时已提升不大。稻秆和麦秆中有超过 95% 的氯元素可以通过水浸法来去除,这说明水浸除氯的效果很好。

2.1.2 温度对钾元素浸出效果影响

稻秆和麦秆中钾元素浸出率随温度以及时间的变化规律如图 2 所示。由图可知,钾元素的浸出规律与氯元素相似。在前半小时内,钾元素浸出速度最快且温度的增加会提高钾元素的浸出速度。相比于稻秆,温度对于麦秆中钾元素浸出的促进作用更加明显,当温度达到 50 °C 时,半小时内钾元素的浸出率较 25 °C 时几乎提高了一倍。浸泡超过半小时后,钾元素的浸出速度明显降低,且随着时间的推移浸出速度还会继续缓慢减小。100 °C 下浸泡 2 h 后,稻秆中钾元素的浸出率几乎不再变化,而麦秆的却仍有一定的增加,这表明此时稻秆中的可溶性钾已几乎完全被浸出,但麦秆中还残留有少许且会随着时间的推移而缓慢浸出。稻秆在 25、50、75 和 100 °C 下浸泡 3 h 后的钾元素浸出率分别为 66.67%、69.34%、81.84% 和 85.12%,相对应的麦秆中钾元素浸出率分别为 59.93%、76.00%、85.87% 和 87.69%。由此可知,温度的提高也有利于钾元素的浸出,虽然其浸出率较氯元素稍低,但超过 85% 的浸出率仍然表明水浸法能够有效地减少生物质中钾元素的含量。

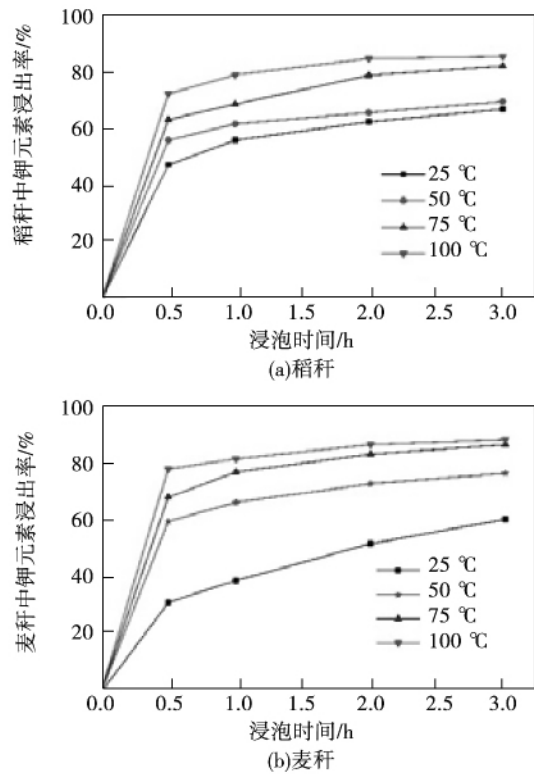


图 2 不同温度下稻秆和麦秆中钾元素浸出率变化

Fig. 2 Changes in leaching rate of K in rice and wheat straw at different temperatures

2.1.3 电镜扫描结果及分析

图 3 所示为麦秆和稻秆分别在 25 和 100 °C 的去离子水中浸泡 3 h 后内表面的微观形貌。由图可知,在 25 °C 时,稻秆和麦秆的内表面均较为完整,而随着温度的升高,3 h 浸泡后内表面逐渐破损,最终出现较多裂纹。虽然生物质中氯和钾主要的存在形式为可溶性盐,但有一部分的氯和钾是被包裹于有机质中而很难被浸出的。所以在浸泡时,前半小时主要为游离态的可溶性的氯和钾的快速溶解,随后即是被有机质包裹的氯和钾元素的缓慢浸出。通过图 3 可知,高温可以破坏生物质细胞的细胞壁,也就是破坏了生物质中纤维素与木质素的结合,这就会加速被其包裹的氯和钾离子的流出,这也应是温度的升高能够促进生物质中氯和钾元素浸出的主要原因。

2.2 酸碱对稻秆和麦秆中氯和钾元素浸出影响

酸碱溶液对麦秆和稻秆中氯元素的浸出率影响如图 4 所示。由图可知,当被 0.25 mol/L 的氢氧化

钠溶液浸泡 3 h 后,麦秆和稻秆中分别有 76.45% 和 65.75% 的氯元素被浸出,均低于同温度下使用去离子水时的 77.91% 和 66.72%,但数值相差很小。这说明氢氧化钠几乎不会影响稻秆和麦秆中氯元素的浸出,浸出率的差距很可能为测量误差所致。当浸泡液为 0.25 mol/L 的柠檬酸溶液时,浸泡 3 h 后,麦秆中氯元素的浸出率仅为 63.33%,明显低于使用

去离子水浸泡时。稻秆中氯元素的浸出率为 66.2%,与使用去离子水浸泡时的效果几乎相同。由此可知,柠檬酸对麦秆中的氯元素浸出有抑制作用,但对稻秆中氯元素的浸出几乎没有影响,造成这一结果的机理尚不明确,还需继续进行深入细致的研究来得出。

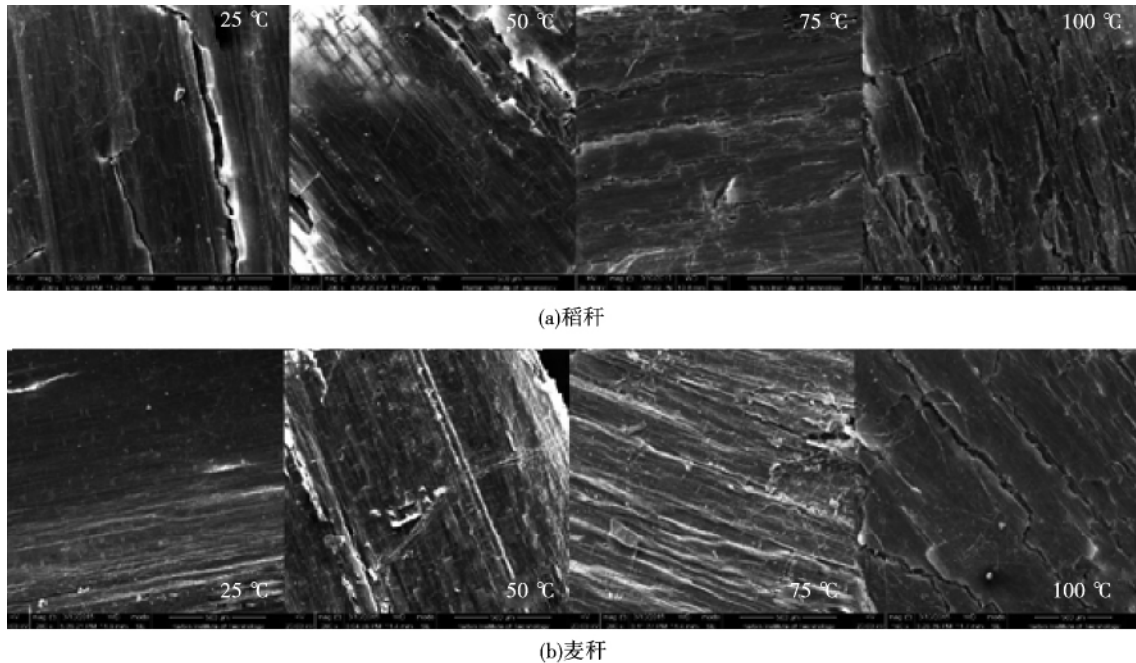


图 3 稻秆和麦秆内表面电镜扫描结果

Fig. 3 Scanning results of the internal surface of rice and wheat straw by using a SEM

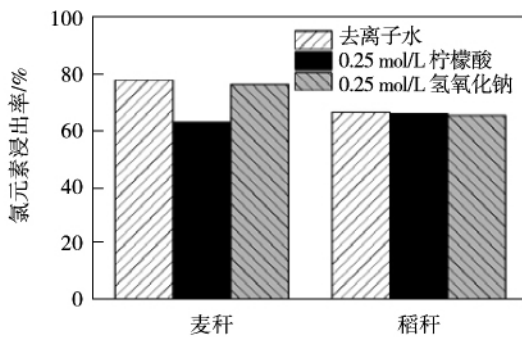


图 4 酸碱对麦秆和稻秆中氯元素浸出率的影响

Fig. 4 Influence of acids and alkalis on the Cl element leaching rate of wheat and rice straw

酸和碱对于麦秆和稻秆中钾元素浸出的影响如图 5 所示。由图 5 可知,浸泡 3 h 后麦秆和稻秆中钾元素的浸出率达到了 74.58% 和 67.74%。相比

于同温度下去离子水作为浸泡液时,浸出率分别高出了 7.91% 和 7.81%,这说明柠檬酸会促进钾离子的浸出。当使用 0.25 mol/L 的氢氧化钠溶液作为浸泡液时,3 h 后麦秆和稻秆中钾元素浸出率分别为 68.42% 和 60.12%,与使用去离子水浸泡时的浸出率几乎相同。由此可知,浓度为 0.25 mol/L 的氢氧化钠溶液对麦秆和稻秆中钾元素的浸出没有影响。

酸碱对稻秆和麦秆内表面微观形貌的影响如图 6 所示。由图可知,当使用酸碱浸泡后,稻秆和麦秆内壁的组织仍然完整,可知浓度为 0.25 mol/L 的氢氧化钠和柠檬酸溶液并不能破坏生物质细胞的细胞壁从而加速氯和钾元素的浸出。柠檬酸能够促进钾元素的浸出的主要原因应为有机酸中的氢离子可以将生物质中的钾离子置换出来,随后置换出来的阴

离子会和有机酸中的酸根阴离子发生反应形成络合物,从而使更多的钾元素被浸出^[19]。

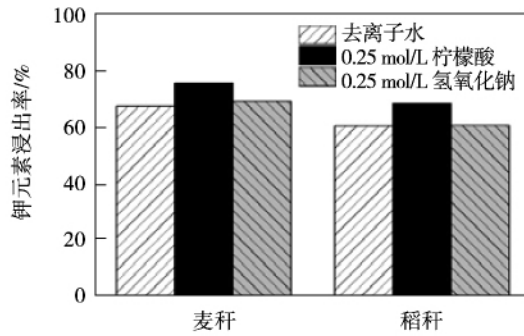


图 5 酸碱对麦秆和稻秆中钾元素浸出率的影响
Fig. 5 Influence of acids and alkalis on the K element leaching rate of wheat and rice straw

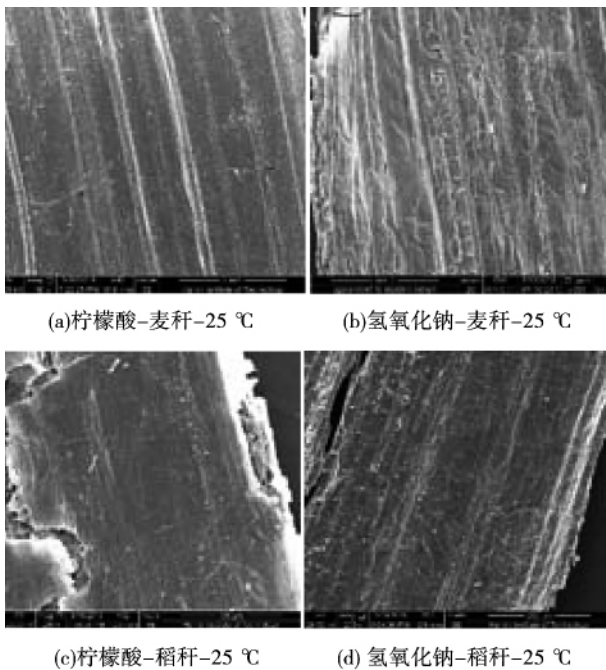


图 6 酸碱浸泡后稻秆和麦秆内电镜扫描结果
Fig. 6 Scanning results of the internal surface of rice and wheat straw by using a SEM after having being immersed in acid and alkali solutions

3 结 论

(1) 稻秆和麦秆中氯和钾元素的浸出规律相似,在所有温度下均是在前半小时内最快,半小时后浸出速度明显减小,且随着时间的推移浸出速度还

会继续缓慢降低。

(2) 浸泡温度的提升能够明显促进氯和钾元素的浸出,特别是当温度达到 75 °C 以上时,效果非常明显,但当温度升高至 100 °C 后的浸出效果较 75 °C 时已提升不大。温度的提高能够促进氯、钾元素浸出的主要原因应为高温破坏了生物质细胞的细胞壁,从而使其中的氯和钾离子流出并溶于浸泡液中。

(3) 水浸法可以有效的减少稻秆和麦秆中的氯和钾元素的含量,在 100 °C 下浸泡 3 h 后,稻秆和麦秆中氯元素的浸出率分别达到 95.18% 和 96.29%,钾元素的浸出率分别达到 81.84% 和 87.69%。

(4) 浓度为 0.25 mol/L 的氢氧化钠溶液对稻秆和麦秆中氯和钾元素的浸出几乎没有影响。浓度为 0.25 mol/L 的柠檬酸溶液会明显抑制麦秆中氯离子的浸出,但不会影响稻秆中氯离子的浸出。此外,柠檬酸中的酸根离子能够与生物质中的钾离子反应形成络合物,从而有效的提高稻秆和麦秆中钾元素的浸出率。

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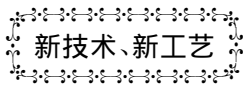
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(刘 瑶 编辑)



程氏热电联产装置为匹配需要可以改变电力和蒸汽的输出量

据《Gas Turbine World》2014年7~8月刊报道,程氏循环(蒸汽回注式)燃气轮机从面世以来已在发电和热电生产中得到广泛应用。

利用燃气轮机排气的余热在余热锅炉中产生蒸汽,蒸汽再回注入燃气轮机,在其中与空气和燃料混合,增加了燃气轮机质量流量,加大了输出功率。

当程氏循环应用于CHP(冷热电联产)装置时,能使CHP装置改变电力和蒸汽产量并在运行过程中满足变负荷的需求。

程氏循环显著地增加旧和改进型F级燃气轮机的输出功率和效率。通过实例比较了6F、7F和9F燃气轮机在设计额定值和性能方面的变化。结果表明,采用程氏循环明显增加了燃气轮机的输出功率和效率。同时,在利用燃气轮机排气余热供热电联产或联合生产使用时,回注蒸汽还可作为供电、供热或供电、供汽之间的一种调节手段。

(吉桂明 摘译)

lished. The pneumatic-hydraulic-servo-elastic coupling software FAST was used to simulate the whole machine dynamic characteristics of the wind turbine under three typical operating conditions and a contrast and analysis were conducted. It has been found that the variation tendency of the torque of the wind wheel is basically in agreement with the power of the wind turbine, thus making the fluctuation in the torque more intense. The dynamic loads exerted on the tower base under various operating conditions differ greatly due to the axial thrust force of the wind wheel affected by the wind speed and wave period, however, the forward and backward bending moment forms the main force-bearing direction. Changes of the swaying and pitching of the platform along the horizontal direction are most intense and waves play an obvious role in restraining the swaying and pitching of the platform. The laws governing changes of the tensile forces of the cable guide device and the anchor with time are most similar and the law governing changes of the maximal tensile force of the mooring cable is in agreement with that of the pitching of the platform. **Key words:** OC₃-Hywind spar platform, floating type wind turbine, numerical simulation, dynamic characteristics

草浆原料的湿法除氯和钾元素试验研究 = **Experimental Study of the Wet Method for Removing Chlorine and Potassium Elements by Using the Straw Black Liquor Raw Material** [刊, 汉] / JI Xiao-yu, CHEN Pei, BIE Ru-shan (College of Energy Science and Engineering, Harbin Institute of Technology, Harbin, China, Post Code: 150001) // Journal of Engineering for Thermal Energy & Power. - 2016, 31(11). - 100 ~ 105

To solve the problem that it is easy for the straw black liquor to agglomerate when burning in a circulating fluidized bed, the wet-method pretreatment procedure was used to reduce the chlorine and potassium content in the black liquor. The deionized water in a range of temperature from 25 °C to 100 °C and sodium hydroxide and citric acid solution at a temperature of 25 °C at a concentration of 0.25 mol/L were chosen respectively to conduct a marination test of rice and wheat straw. In this connection, a liquid chromatograph mass spectrometer (LC-MS) and an inductively coupled plasma optical emission spectrometer (ICP-OES) were employed to measure the chlorine and potassium ion concentration in the marination solution and a scanning electronic microscope was applied to observe the microscopic structure of the rice and wheat straw on the surface having been marinated under various conditions. The influence of the marination time, temperature and acids and alkalis on the lixiviation rate of chlorine and potassium element in the biomass observed. It has been found that to raise the marination temperature can destroy the cell wall of the biomass, thus promoting the lixiviation of chlorine and potassium in the rice and wheat straw. The sodium hydroxide solution at a concentration of 0.25 mol/L will have almost no influence on the lixiviation of chlorine and potassium in the rice and wheat straw. The citric acid solution at a concentration of 0.25 mol/L will restrain the lixiviation of chlorine in the wheat straw, however, will have almost no influence on the lixiviation of chlorine in the rice straw. In addition, the citric acid solution at a concentration of 0.25 mol/L will effectively enhance the lixiviation rate of potassium element in the rice and wheat straw. The water lixiviation method will have a very good result to remove chlorine and potassium element. After three hour lixiviation at 100 °C, the lixiviation rate of chlorine and

potassium element will exceed 95.18% and 85.12% respectively. **Key words:** wet method pretreatment, chlorine and potassium element, lixiviation rate, citric acid, sodium hydroxide

生物质电厂 3 种管材的耐腐蚀研究及爆管分析 = **Study of the Corrosion-resistant Performance of Tubes in a Superheater in a Biomass Power Plant and Analysis of the Tube-rupture-caused Corrosion** [刊, 汉] / ZHANG Hong-liang, LIU Zi-han (Chemistry Research Institute, Electric Power Science Academy, Guangdong Power Grid Co. Ltd., Guangzhou, China, Post Code: 510080), LI Yu-chun, WANG Wei (College of Chemical and Biological Engineering, Changsha University of Science and Technology, Changsha, China, Post Code: 410114) // Journal of Engineering for Thermal Energy & Power. -2016, 31(11). -106 ~ 111

A high temperature oxidation dynamics experimental study and a high temperature corrosion dynamics study were performed of the main materials of the tubes in a superheater in a biomass power plant, their features in high temperature corrosion were analyzed and on this basis, the cases of tube rupture at the site of the biomass power plant were tested and analyzed. It has been found that the rupture of tubes in the superheater in the biomass power plant is caused by the material at the outside of tubes directly corroded by strong corrosive alkali metal chloride, forming ashes having a low melting point to accelerate an advance damage to the material. In addition of the high temperature creep and a deterioration in the quality of steam in a short time period etc. factors, the rupture of tubes in the superheater results eventually. On the basis of the features of relevant influencing factors being analyzed, pertinent material protection methods were proposed. **Key words:** biomass power plant, superheater, alkali metal chloride, tube rupture, protection method

燃煤烟气体积热值比的提出及应用 = **Putting-forward and Applications of the Volume and Heating Value Ratio of Flue Gases Produced in Combustion of Coal** [刊, 汉] / ZHANG Jin-zhu, JI Jin-fang, LIANG Xin-lei, SHANG Yong-qiang (Huadian Zhengzhou Mechanical Design Research Institute Co. Ltd., Zhengzhou, China, Post Code: 450015) // Journal of Engineering for Thermal Energy & Power. -2016, 31(11). -112 ~ 115

Recently, the ultra low emissions are required in thermal power plants in China, the performance of flue gas environmental protection equipment items at the tail portion of existing boilers are requested to be improved continuously and an even higher standard for design of environmental protection equipment items is proposed. As an important parameter, the flue gas flow speed seems more and more important. Through an analysis of coal burned, a ratio between the flue gas volume and the heating value of coal burned was proposed, i. e. a ratio between the flue gas volume produced by each kilogram of coal burned and the as-received basis low heating value. Through this ratio, one can know clearly the flue gas volume produced by various coal ranks. In the design process, through calculating the volume and heating value ratio of coal burned, one can make a judgement whether the flue gas volume adopted in the design of a project is excessively small or large, therefore offering guidance for subsequently choosing the allowance of the flue gas volume in type selection of equipment items. **Key words:** coal combustion, flue gas volume and heating value ratio, flue gas flow rate, allowance, low heating value