

麦草木质素水泥混凝土减水剂研究*

樊耀波 穆环珍 徐良才 范秀英

张士强

高国义 单文华

(中国科学院环境评价部, 北京 100085)

(北京市海淀区水泥厂)

(国家建筑材料测试中心)

摘要 将从麦草造纸黑液中提取的木质素进行磺化改性, 探索其作为水泥混凝土减水剂的可行性。研制了 ZS-3 号减水剂。同时对麦草造纸黑液资源化治理工艺中产生的含磺化木质素多糖液进行了水泥混凝土减水性能实验。研制了 ZS-2 号减水剂。实验结果表明, ZS-3 使水泥混凝土减水率达 10%, 7 d 抗压强度增加 18%, 28 d 抗压强度增加 5%, 达到水泥混凝土普通减水剂性能。ZS-2 使水泥混凝土减水率达 10%, 7 d 抗压强度增加 73%, 28 d 抗压强度增加 26%, 达到水泥混凝土高效减水剂性能。

关键词 麦草木质素, 磺化, 混凝土减水剂。

麦草原料制浆黑液中含有大量的木质素。但这些木质素目前大多随黑液排放。造成资源的浪费和对环境的严重污染。开展麦草木质素水泥混凝土减水剂(以下简称减水剂)的研究, 可增加减水剂产量, 缓解我国减水剂供需矛盾又可推动我国中小造纸麦草浆黑液资源化治理工作的进展。目前, 国内已有人作过这方面工作, 即直接对黑液进行处理制造减水剂^[1-3]。本研究是对提纯的麦草木质素进行磺化改性制成减水剂。该麦草木质素按中国科学院环境评价部麦草黑液资源化治理技术提取。经该技术分离出的多糖液含有一定量的磺化木质素。

1 实验

1.1 麦草木质素的磺化

将木质素在 $\text{pH} \geq 11$ 条件下溶解, 在 70℃ 条件下加入甲醛进行甲基化反应, 反应时间 2 h。然后, 在 170℃ 条件下加入磺化剂 Na_2SO_3 进行磺化反应。在磺化实验中选择时间, 配比, 温度、压力等反应控制参数。采用水泥净浆流动度指标判定各批反应产物的磺化效果。最后从 13 批实验中选出最佳水泥混凝土减水剂样品。即对水泥有最大分散能力者(水泥净浆流动度最大)。这种磺化木质素水泥混凝土减水剂取名为 ZS-3。

1.2 含磺化木质素多糖液的制备

含磺化木质素多糖液是麦草黑液资源化治

理技术分离出的一种产物。经实验测定其含一定量的磺化木质素。将该产物分析其固形物含量及成分然后进行水泥混凝土减水性能指标测定。该物质被取名为 ZS-2 减水剂。

1.3 减水性能测定及应用条件研究

减水性能选择水泥净浆流动度、砂浆减水率、混凝土减水率、混凝土抗压强度等指标。

水泥净浆流动度的测定参考标准方法^[4]自制模具进行。测定中保持条件、步骤的一致性结果是结果可靠的关键。水泥砂浆减水率由北京市海淀区水泥厂测定。混凝土减水剂性能指标测定由中国建材研究院建材测试中心进行。混凝土实验按 GB8076-87《混凝土外加剂》的国家标准进行。

2 结果与讨论

ZS-2 外观黑稠, pH 为 9。据文献资料及本次实测结果计算, ZS-2 的化学成分见表 1。ZS-3 为黑色液体, pH 约 10, 其化学成分见表 1。ZS-2、ZS-3 均为可溶性物质, 以强酸条件下也无沉淀物出现。

经实验得知, 在减水剂样品的磺化时间一定时, 其水泥净浆流动度随加入磺化剂的比例增加而升高(见表 2)。但当磺化剂加量达到

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表 1 ZS-2、ZS-3 化学成分

ZS-2		ZS-3	
化学成分	含量 ¹⁾ (%)	化学成分	含量 ¹⁾ (%)
磺化木质素	8	磺化木质素	57.3
多缩戊糖	24	甲醛	0.9
其它有机物	18	氢氧化钠	2.4
无机盐	50	亚硫酸钠	20.5
		其它成分	18.5
合 计	100	合计	100.0

1) 指各成分固形物占总固形物之比

6 mol/kg 木质素时流动度不再增加。表 2 基准点流动率 7.0 cm 指不加 ZS-3 的水泥净浆流动度。从表 2 中数据可以看出加 ZS-3 后流动度增加一倍多,反映 ZS-3 对水泥有较强的分散能力。此分散能力越强,水泥混凝土的减水效果越好。

样品磺化时间对水泥净浆流动度的影响情况见表 3。从表 3 可知,水泥净浆流动度随磺化时间的增加而增加,但反应 4 h 小时后 ZS-3 的水泥扩散能力不再增加。

表 2 ZS-3 水泥净浆流动度¹⁾(不同磺化剂加量)

样品编号	磺化剂加量 (mol/kg 木素)	掺量 (%)	流动度 (cm)
基 准	0	0.00	7.0
ZS-3-1	1	2.28	15.3
ZS-3-2	2	2.28	16.0
ZS-3-3	3	2.28	16.1
ZS-3-5	5	2.28	16.2
ZS-3-6	6	2.28	16.3
ZS-3-7	7	2.28	16.3

1) 掺量指样品与水泥重量之比,采用 325[#] 矿渣硅酸盐水泥

表 3 ZS-3 水泥净浆流动度¹⁾(不同磺化时间)

磺化时间 (h)	掺量 (%)	流动度 (cm)
1	2.28	16.6
2	2.28	
3	2.28	17.0
4	2.28	17.2
5	2.28	17.2

1) 同表 2 注

在选择出最佳减水剂样品的基础上,进行了 ZS-3、ZS-2 水泥砂浆减水实验及水泥混凝土减水与强度实验。水泥的砂浆减水率见图 1。图

1 表明,2 种减水剂样品都具有明显减水作用。ZS-2 在掺量<2‰无减水作用,而在掺量达 7‰以上才出现较好减水效果。ZS-3 在掺量很小时就表现出较强的减水作用,在掺量 7‰时达到最大值。这一结果为以后的混凝土减水实验提供了选择掺量的参考依据。

混凝土减水剂是混凝土外加剂的一种。其性能与质量最终要根据国家标准 BG8076-87《混凝土外加剂》来评定。按国标规范要求 ZS-2、ZS-3 经中国建筑材料研究院国家建筑材料测试中心测定其减水性能,测定结果见表 4。表 4 表明,ZS-2 达到高效减水剂合格品标准。ZS-3 基本达到普通减水剂合格品标准,从减水率看 ZS-3 优于普通减水剂合格品要求。

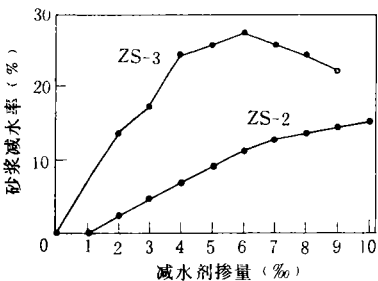


图 1 减水剂砂浆减水率与掺量关系

在混凝土的减水试验中发现 ZS-2、ZS-3 都存在引气问题。其中 ZS-3 引气量较大,影响了掺量的增加,使其减水率大的特点难以发挥。引气量大使混凝土含气量大,强度下降。因此,以上减水实验结果是掺入一定消泡剂的条件下获得的。实验中加入的消泡剂为磷酸二丁酯。经反复实验,ZS-2 使用时消泡剂掺入量占水泥用量的 5×10^{-5} ,减水剂最佳掺量是水泥用量的 7‰。ZS-3 最佳掺量是水泥用量的 1‰,消泡剂掺入量占水泥用量的 2×10^{-5} 。

水泥混凝土减水剂 ZS-2、ZS-3 是一种阴离子型含亲水及疏水基团的物质,具有表面活性。它们的引气问题与其纯度、分子量大小、分子结构有关^[5]。引气机理还有待更系统研究工作。

3 结论

(1) ZS-2 减水率可达 10%,7 d 抗压强度

表 4 水泥混凝土减水剂抗压强度实验结果¹⁾

试 样	掺量 (%)	水灰比	减水率 (%)	含气量 (%)	坍落度 (cm)	7d		28 d	
						抗压强度 (kg/cm ²)	增强率 (%)	抗压强度 (kg/cm ²)	增强率 (%)
基准	0.0	0.59	0.0	1.1	6	251	100	411	100
ZS-2	7.0	0.53	10.0	1.9	5	433	173	518	126
ZS-3	1.05	0.52	11.2	2.8	4	295	118	432	105
GB8076-87									
普通合格品			≥5	≤4	6±1		≥110		≥105
普通一级品			≥8	≤3	6±1		≥115		≥110
高效合格品			≥10	≤4	6±1		≥120		≥115
高效一级品			≥12	≤3	6±1		≥125		≥120

1) 品级指国标 GB8076-87《混凝土外加剂》的普通减水剂和高效减水剂标准

可增加 73%，28 d 抗压强度可增加 26%。ZS-2 件以研制出更高效的水泥混凝土减水剂。是造纸黑液的资源化再生利用产品，成本低，具有明显实用价值。

(2) 麦草木质素经磺甲基化反应可制成减水率大于 10% 的普通水泥混凝土减水剂，取名 ZS-3。其 7 d 水泥混凝土抗压强度增加 18%，28 d 抗压强度增加 5%。

(3) 提高减水率，降低引气量是提高减水剂性能的关键。ZS-3 引气性较大影响了其减水能力的发挥。有必要改进麦草木质素的磺化条

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表 10 几种木质素的主要物理化学特性及对小麦发芽率的影响

分 析 项 目 ¹⁾	山西晋城硫酸木素	河北涿州二氧化硫木素	山东沂源二氧化硫木素
羧基含量(%)	6.3707	3.7985	1.9602
C/H(分子共轭度)	1.19	1.17	1.17
E ₄ /E ₆ (芳环缩合度)	4.19	4.88	4.56
Zn(%)	431×10 ⁻⁴	353×10 ⁻⁴	62.5×10 ⁻⁴
B(%)	61×10 ⁻⁴	42×10 ⁻⁴	9.9×10 ⁻⁴
Mo(%)	269×10 ⁻⁴	11.2×10 ⁻⁴	<0.5×10 ⁻⁴
S(%)	0.835	2.04	3.12
1050 cm ⁻¹ ×100 吸收强度	0	71	70
—OCH ₃ 质子百分比(%)	16.9	18.5	20.2
结构单元类型	HGS ¹⁾	HGS	GHS
小麦 437 号发芽率(%)	100	70	55

1) H 为 3-(4-羟基苯基)-2-丙烯-1-醇; C 为 3-(3-甲氧基-4-羟基苯基)-2-丙烯-1-醇; S 为 3-(3, 5-二甲氧基-4-羟基苯基)-2-丙烯-1-醇

(3) 经试验木质素的拌种量为种子重量的 0.4%，pH7.8 左右。

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matter to form chloroform, the production of which increases with an increase in COD, pH, and chlorine dosage. The level of chloroform would exceed the national drinking water quality standard ($60 \mu\text{g/L}$), 48 hours after dosing 7 mg/L chlorine to water with a COD of 3 mg/L chlorine dioxide does not react with organic matter to form chloroform. After adding 11.33 mg/L of chlorine dioxide to a water having a COD of 2.67 mg/L for 48 hours, the level of chloroform was below detection limit. Moreover, a combined use of chlorine dioxide and chlorine can inhibit the formation of chloroform. However, chlorine dioxide was not able to remove chloroform already present in water.

Key words: chlorine dioxide, water disinfection, chloroform.

Study on the Degradation of DNA in an Acidic Medium by HPLC Using Gradient Elution. Long Yaotin et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **16** (3), 1995, pp. 35–38

The determination and separation of bases from the degradation products of DNA in hydrochloric acid, perchloric acid, trichloroacetic acid, trifluoroacetic acid and formic acid were described. The hydrolysis yields of DNA adduct products of MNU also were presented. The effects of mobile phase composition, flow rate, column temperature, gradient ramp, pH value, salt concentration, and buffer concentration on capacity factors (K') were respectively discussed. The experimental results showed that hydrochloric acid is a favorable hydrolytical medium for DNA degradation and high recovery of DNA bases can be obtained. The optimum hydrolytical conditions for adduct products of DNA of MNU were 1 mol/L hydrochloric acid, 20 min, and $80\text{--}100^\circ\text{C}$.

Key words: HPLC, DNA, MNU, adduct.

A Study on Technology for Solidification of Pulverized-Coal Ash and Its Application. Guo Qingyun (Nanjing Institute of Environmental Protection Science for Electric Power, Ministry of Electricity Industry, Nanjing 210031); *Chin. J. Environ. Sci.*, **16**(4) 1995, pp. 39–41

Test and research have been made on a solidification technology for pulverized ash to be used in suppressing dust of ash ponds or landfills for coal-fired power plants. As a result, two series of ash-stabilizing agent have been already developed. The solidified ash has a compressive strength over

16 kg/cm^2 , with a maximum of 70 kg/cm^2 , and stability coefficients in water and in freezing state are over 0.90 and even up to 1.00. This process is highly efficient in dust suppression, durable in operation, low in cost, abundant in raw material supply, simple in application, and easy in popularization. It can be used for ash ponds or landfills in operation or being full, for reinforcing ash dykes and for preventing permeation of ash ponds.

Key words: solidification technology, pulverized-coal ash, stabilizing agent, stability coefficients.

Preliminary Study on the Biological Effects of Lignin Dressing Seed on Plant Growth. Fan Xiuying et al. (EIA Unit, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 42–45

Lignin, extracted from the black liquor discharged from small and medium-sized pulp and paper mills, was used as a seed dressing agent to coat seeds at a rate of 0.4% by weight of seed and at pH 7.8, and the dressed seeds were grown in experimental plots containing a sand and soil culture and in fields. The results show that the seed dressing increased the rate of seed germination, accelerated the development of root systems, enhanced the effective tillering of wheat, increased the resistance to drought and to pests, the number of seeds in a single ear, and the weight per thousand seeds, and thus raised the yield. The treated wheat and maize grown in all experimental fields in Shandong and Hebei provinces and in Beijing were found to have an over 10% increase in yield as compared to control. The biological effects of seed dressing were found to be closely related to the process of extracting lignin from black liquor, the source of pulping raw materials, the rate of dressing agent used, the pH value of dressing solution, the variety of crops and the fertility of soil. The cost of lignin as a seed dressing agent is low due to its being from pulping waste and the dressing technology is quite simple, environmentally sound and easy to be diffused for agricultural purpose.

Key words: lignin, pulping waste, waste recycle, seed dressing agent, wheat, maize.

Development of A Concrete Water-Reducing Admixture Using Lignin from Alkaline Wheat Straw Pulping Black Liquor. Fan Yaopo et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **16**(4), 1995,

pp. 46—48

Lignin extracted from an alkaline wheat straw pulping black liquor was modified by sulfonation to study the feasibility of its use as a concrete water-reducing agent. This has resulted in the development of ZS-3 water-reducing admixture. In addition, a liquor containing sulfonated lignin and polysaccharides from the conversion process of wheat straw pulping black liquor was found to have a function of concrete water reduction and was turned into a superplasticizer ZS-2. Both ZS-3 and ZS-2 had a water reduction by 10%. The compressive strength of concrete was increased by 18% (7 days) or 5% (28 days) when ZS-3 was added, and by 73% (7 days) or 2% (28 days) when ZS-2 was added.

Key words: concrete water-reducing admixture, wheat straw lignin, sulfonation.

Small-Sized Non-Sludge-Discharged Sewage Treatment and Reuse System. Chen Xueyi et al. (Weifang Bestec Environmental Protection Engineering Development Co., Ltd., Weifang 261011); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 49—50

A small-sized sewage treatment and reuse system without sludge discharge has been developed, based on a process consisting of two stages of contact anaerobic filters, two stages of contact aerobic filters, a slow sand filter and a fast sand filter. Generally, a domestic sewage can be treated through this system to give a satisfactory effluent, with a BOD removal of 91.7%, a COD removal of 88.9%, a SS removal of 91.1%, and a total P removal of up to 43.5%.

Key words: excess sludge, anaerobic treatment, aerobic treatment.

Determination of Chlordimeform Residues in Rice by Enzyme Immunoassay Using Monoclonal Antibody. Yu Wanjun et al. (West China University of Medical Sciences, Chengdu 610041); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 51—53

Three sensitive enzyme-linked immunosorbent assays (ELISAs)—indirect competitive ELISA, direct competitive ELISA, and reverse direct competitive ELISA—with immobilized antibody were developed for the determination of chlordimeform residues in rice. Their IC_{50} are of 1.3, 1.7 and 5.3 ng/ml, respectively. Samples were homogenized with methanol in a blender or in an ultrasonic disintegrator. The extracts could be measured directly after dilution, or underwent

a simple clean up procedure, which could improve the accuracy of the ELISAs. Effects of pH in the reaction medium, the incubation temperature, the extracting agent and the sample matrix on the detection sensitivities were also studied and discussed.

Key words: chlordimeform, pesticide residue analysis, enzyme-linked immunosorbent assay (ELISA).

Synchronous Scanning Derivative Spectrofluorimetry for the Determination of Selenium with 2, 3-Diaminophthalene. Zhao Zhenhua et al. (Beijing Municipal Research Academy of Environmental Protection, Beijing 100037); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 54—56

The synchronous fluorescence spectra of fluorescent chelate of selenium with 2, 3-diaminophthalene (DAN) and its synchronous scanning derivative spectra were studied. The specific $\Delta\lambda$ of the synchronous spectra was found to be 140 nm. The first derivative spectrofluorimetry for the determination of selenium with DAN was described. The limits of detection were 1.5, 1.9 and 3.0 for the first derivative, second derivative and normal spectrofluorimetric technique, respectively. Coefficient of variation was 6.7 for the first derivative spectrofluorimetry, and 9.2 for the normal spectrofluorimetry.

Key words: selenium, synchronous spectrofluorimetry, derivative spectrofluorimetry.

Determination of Total Organic Halogen (TOX) in Water. Zou Huixian et al. (Dept. of Environ. Sci. and Eng., Nanjing Univ., Nanjing 210093); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 57—60

A modified determination method for TOX was described, whereby purgeable and nonpurgeable fractions were measured respectively. Purgeable organic halogen (POX) was stripped with a mixture of N_2 and O_2 ; and nonpurgeable organic halogen (NPOX) was enriched with a Liquid-liquid Extraction (LLE) method. Both were introduced into a combustion system to change them into X^- , which were then determined with spectrophotometry. There was a detection limit of about 1 $\mu\text{mol/L}$, a variation coefficient of less than 3%, with an average recovery of 81% for 10 model compounds. The TOX concentration in the tap water from Jiangsu province was from about 217 to 483 $\mu\text{g/L}$.

Key words: purgeable organic halogen, non-purgeable organic halogen, total organic halogen,