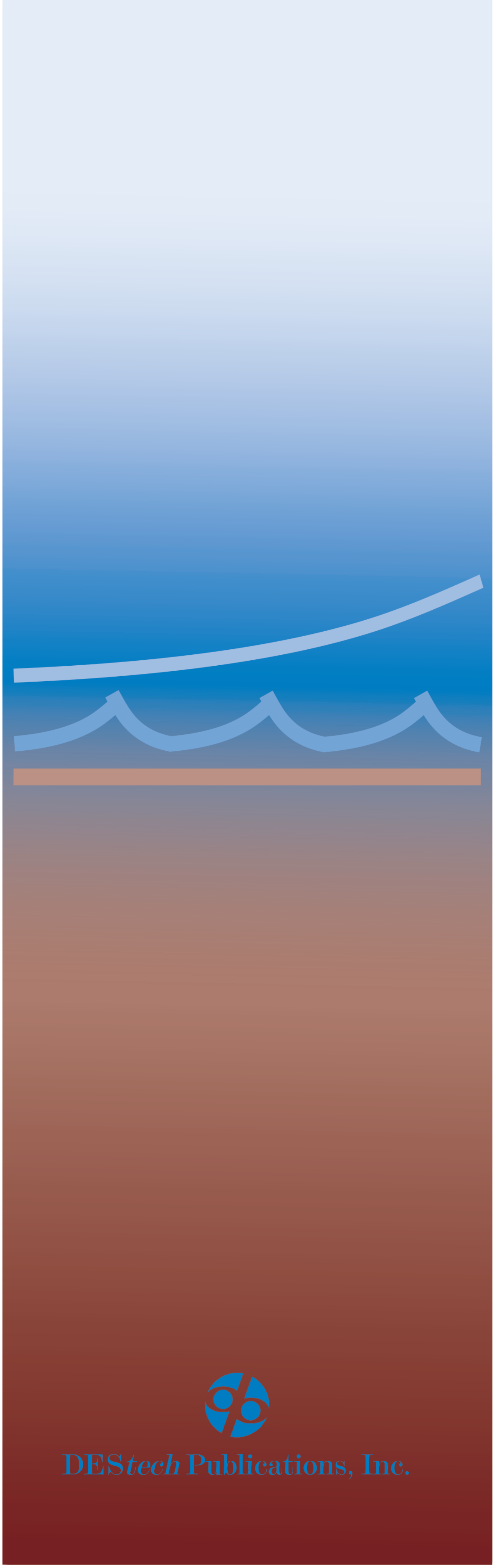

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The objective of the *Journal of Residuals Science & Technology* (JRS&T) is to provide a forum for technical research on the management and disposal of residuals from pollution control activities. The Journal publishes papers that examine the characteristics, effects, and management principles of various residuals from such sources as wastewater treatment, water treatment, air pollution control, hazardous waste treatment, solid waste, industrial waste treatment, and other pollution control activities. Papers on health and the environmental effects of residuals production, management, and disposal are also welcome.

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pduncan@unt.edu

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Carleton University, Canada
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ludovico.spinosa@fastwebnet.it

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aarne.vesilind@gmail.com

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The Effectiveness of Acid Fermentation of Sonicated Primary Sludge

J. BIEŃ, T. KAMIZELA, M. KOWALCZYK, A. GROSSER, N. ZWIERZ and M. ZABOCHNICKA-ŚWIĄTEK*
[1]*Institute of Environmental Engineering, Czestochowa University of Technology, Brzeźnicka 60a, 420-200 Częstochowa, Poland*

ABSTRACT: The high effectiveness of biological processes of phosphorus removal and denitrification requires the presence of easily assimilable carbon, especially volatile fatty acids in wastewater. One of the method of intensification of biological phosphorus removal is obtaining volatile fatty acids from primary sludge in the process of acid fermentation. The main objective of the study was to determine the applicability of sonication as a method of intensifying the acidic fermentation. The results confirmed that sonication affects the decomposition of organic matter contained in the primary sludge; however, it is necessary to further optimize the presented method.

1. INTRODUCTION

BIOLOGICAL NUTRIENT REMOVAL (BNR) is an effective wastewater treatment technique, which is currently used on a global scale. For biological removal of total phosphorus and nitrogen, volatile fatty acids (VFAs) are required. However, sufficient concentration of VFAs is not always available in wastewater. For this reason, it is necessary to add an easily biodegradable carbon source to the treatment process to fulfill effluent demands for removal of nutrients with biological processes. The potential source of readily biodegradable organic matter could be compounds produced during acid fermentation of primary sludge [1,2].

Acid fermentation of primary sludge could be realized as in-line and side-stream prefermentation in an activated primary tank. In-line process consists in allowing settled raw sludge solids to accumulate in the bottom of the primary settler tanks and recycling partially this sludge to elutriate the fermentation products out of the sludge. The side-stream prefermentation is a two-stage operation. The settled sludge is conducted to the fermentation unit and the fermented sludge is returned to the primary settler to elutriate the VFAs with the influent wastewater [3,4]. Major operational factors influencing the fermentation process in an activated primary tank include the settleable solids, suspended solids and total solids loading, the sludge age or sludge retention time, and the sludge elutriation rate, which is obtained from the sludge recycle rate [5]. The efficiency of VFAs production in the side-stream prefermentation is also affected by a number of factors, including e.g. solids concentration, agitation, hydraulic retention time and temperature [6,7].

The essence of primary sludge fermentation is partial conversion of the settled solids into soluble and mostly readily biodegradable components, especially VFAs. Prefermentation refers to the first phase of anaerobic biodegradation. This phase consists of two sequential processes, namely hydrolysis and acidogenesis. Hydrolysis breaks down particulate or high molecular weight soluble organic compounds into simpler soluble molecules [8].

The rate-limiting step of this biological process is organic matter hydrolysis. Various pretreatment methods can be used to accelerate hydrolysis or improve sludge anaerobic degradability. These methods include mechanical (ultrasonic treatment, lysis-centrifuge, liquid shear and grinding), thermal, and chemical techniques, as well as their combinations; also, biological interventions to the feedstock and enzymatic methods may be used [9].

Ultrasonic wave propagation called sonication plays role as a factor supporting the traditional methods of wastewater treatment and sludge treatment. However, the dominant application area of sonication is the sewage sludge processing in anaerobic stabilization process. Through the use of ultrasonic disintegration is obtained: increase biogas production, enhance the solubility of sludge solids, which become better accessible to the anaerobic bacteria, the suppression of foaming as well as reduction of organic matter [10,11].

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*Author to whom correspondence should be addressed.
E-mail: mzabochnicka@is.pcz.czest.pl

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Acoustic wave propagation generates acoustic cavitation with extremely high local temperatures and pressures. According to Foladori *et al.* [12], Gogate and Kabadi [13] and Kidak *et al.* [14], sewage sludge disintegration process in the ultrasonic field can be caused by hydro-mechanical shear forces (this mechanical action produced by cavitation is the most effective at frequencies bellow 100 kHz-optimum at 20 kHz); oxidizing effect of radicals (the highest efficiency of sonochemical reactions was observed at more than 100 kHz), thermal decomposition/breakdown of volatile hydrophobic substances in the bioslids as well as increase of temperature during ultrasonic sludge disintegration. Therefore, the physical and chemical effects of ultrasonic waves propagation represent a very wide application potential of sonication.

This work demonstrates the possibilities of ultrasound application to intensification of acid fermentation of primary sludge. It was assumed that ultrasonic wave propagation will lead to breakdown the floc structure and the cell wall of microorganisms contained in the primary sludge. This homogenizing and disintegrating impact of sonication was used to the acceleration of hydrolysis phase of acid fermentation.

2. MATERIALS AND METHODS

2.1. Materials

Sewage sludge was collected from a municipal wastewater treatment plant (Silesia Region, Poland). The treatment plant is a BNR facility serving 330,000 people. The primary sludge (PS) was obtained from the sludge hopper of primary settling tank. The inoculum (IN) was collected from the digester or the sludge hopper of primary settling tank (if inoculum was untreated primary sludge). A summary of important characteristics of the sludge used in the experiments are presented in Table 1.

Table 1. Characteristics of Sludge Used in Studies.

Characteristics of Sludge	**Primary Sludge (PS)**	**Inoculum (IN)**
pH	6.55–7.48	7.89–8.25
Alkalinity, A (mgCaCO$_3$/L)	642–725	2650–2867
Volatile fatty acids, VFAs (mgCH$_3$COOH/L)	1214–1700	721–586
Ammonium nitrogen, NH$_4$-N (mg N-NH$_4^+$/L)	82–93	620–668
Total solids, TS (g/L)	38.2–51.7	17.3–18.4
Volatile solids, VS (g/L)	28.1–42.4	9.6–9.9

2.2. Sonication

Sonication was carried out with low-frequency (20 kHz) ultrasonic processors: VC750 and VC 1500 (Sonics, USA). Samples with a volume of one liter were sonicated at ambient temperature. Cross-sectional area for the sonication vessel was A = 78.5 cm^2. In the study two amplitude classes were tested, namely A_1 = 61.0 µm (VC750) and A_2 = 39.0 µm. The acoustic energy (E) delivered to the sample was adjusted by varying the sonication time (t_S). Sonication with an ultrasonic processor VC750 was performed for 600 and 1200 s. While in the second ultrasonic processor sonication was performed for 300 and 600 s. The energy supplied to the mass unit (specific energy – E_S) was calculated by Equation (1).

$$E_S = \frac{E}{V_S \times TS}, \text{ kJ/kg}TS \qquad (1)$$

Where:

E = amount of acoustic energy (watts × seconds) that is being delivered to the probe (energy monitor of ultrasonic processor), J
E_S = specific energy, kJ/kgTS
TS = total solids concentration in samples, g/L
V_S = sample volume, L

2.3. Experimental setup

The study was performed in three stages. In a first stage the VC750 ultrasonic processor VC 750 was used (Stage I). In the second stage the ultrasonic wave was generated by the VC1500 processor (Stage II). Based on these results the second stage was conducted in order to evaluate the biodegradation efficiency of sewage sludge and GTW mixtures depending on co-substrate ratios.

Based on the results obtained in these stages were determined parameters of ultrasonic field (amplitude and sonification time) for the third stage (Stage III). The aim of the third stage was to investigate the transfer of research results obtained in Stage I and II for Stage III scale. Experiments in one and second stage were performed in triplicate in 500 ml bottles with working liquid volume of 300 mL at 37°C. Once a day the bottles were mixed by hand.

The experiment's third stage was carried out in three glass reactors with a liquid volume of 6 L operating at a controlled mesophilic temperature of 37°C. The

Table 2. Experimental Procedure—Applied Research Combination.

Sample No.	Primary Sludge	Amplitude, μm	Sonication Time, s	Inoculum PS/IN, v/v	Specific Energy, kJ/kg TS	Reactor Type
Stage I						
1	Untreated (control)	–	–	1:10	–	bottle
2	Sonicated	61.0	600	1:10	1900.0 ± 111	bottle
3	Sonicated	61.0	1200	1:10	3790.0 ± 194	bottle
Stage II						
4	Untreated (control)	–	–		–	bottle
5	Sonicated	39.0	600		2740 ± 252	bottle
6	Sonicated	39.0	1200		5300 ± 401	bottle
Stage III						
7	Untreated (control)	–	–	1:10	–	reactor
8	Sonicated	61.0	1200	1:10*	3610 ± 206	reactor
9	Sonicated	61.0	1200	1:10	3610 ± 206	reactor

*Untreated primary sludge was used as inoculum.

temperature was controlled by a thermostatically regulated water bath. The reactor was constantly mixed (180 rpm) by a mechanical stirrer. General information about experimental procedure is given in Table 2.

2.4. Analytical Methods

The following parameters were analyzed to characterize the influent and effluent streams: total solids (TS), volatile solids (VS), volatile fatty acids (VFA) (steam distillation - BÜCHI K-355), ammonia nitrogen (NH_4-N), pH and alkalinity. All analyses were conducted according to Standard Methods [15]. All parameters were measured in triplicates.

3. RESULTS

3.1. Results of Stage I

The most important analytical parameter in all stages was the concentration of VFAs. During this stage to 4 days in all samples the concentration of volatile fatty acids remained at a similar level. After this time threshold the sonicated sludge (sample 2, 3) was characterized by a concentration of VFAs about 1000 mg/L greater than in the control (sample 1), (Figure 1). For alkalinity significant differences between the samples (1–3) were observed (Figure 1). In principle changes in the alkalinity of samples are caused by the decom-

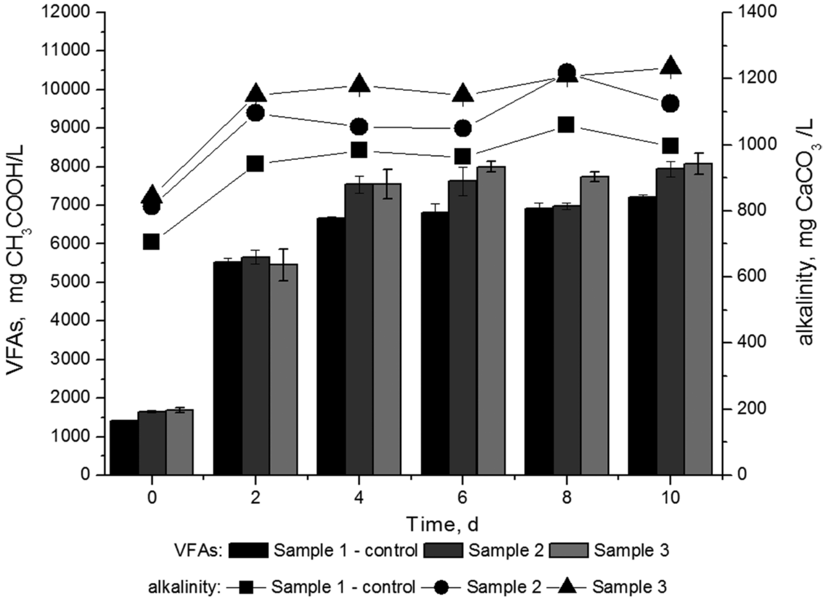

***Figure 1.** Variation of VFAs concentration and alkalinity during acid fermentation in first stage.*

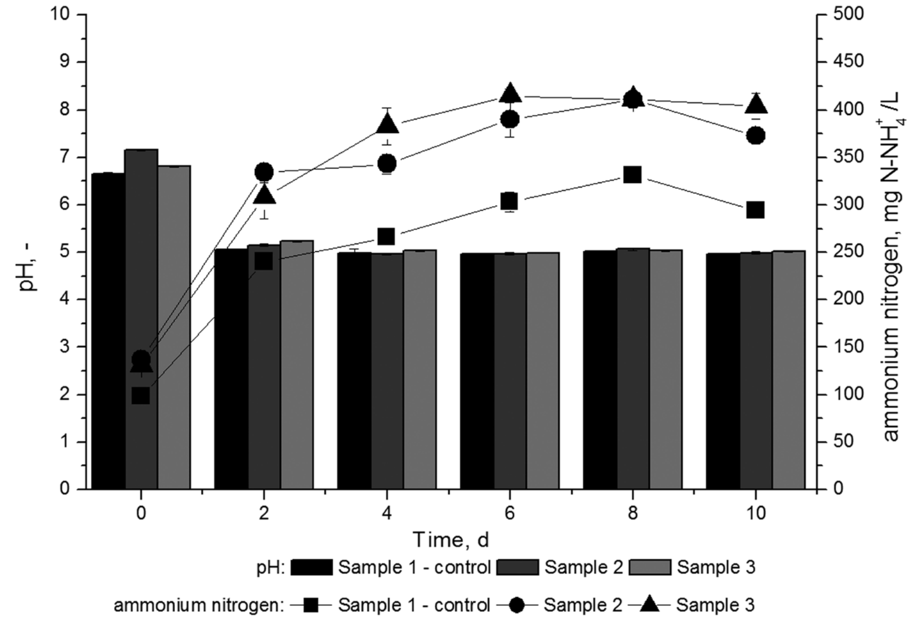

Figure 2. *Variations of pH and ammonium nitrogen during acid fermentation in first stage.*

position of organic matter under anaerobic conditions. In sonicated samples was noted intensification of biochemical transformations, especially for a 20 minute exposure time.

During experiment in first stage the alkalinity of sonicated samples was about 150 mg/L greater than in the control. In all samples, compared to initial values the decrease pH was observed (Figure 2). The highest decrease of parameter was observed in the first days of digestion.

In the following days of the process, pH remained at comparable level (5 ± 0.1). During the study, up to the fifth day, increase the concentration of ammonia nitrogen was observed (Figure 2). After this time, in the control sample values stabilized at around 300 mg/L and 400 mg/L for mixtures containing sonicated sludge (sample 2, 3).

3.2. Results of Stage II

A common feature of sludge samples examined in second stage was almost identical course of changes

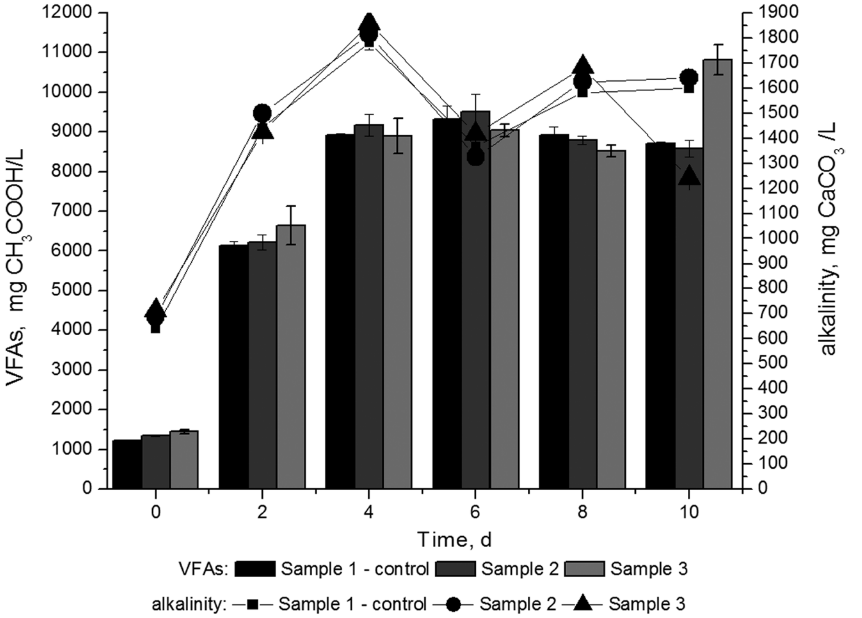

Figure 3. *Variation of VFAs concentration and alkalinity during acid fermentation in second stage.*

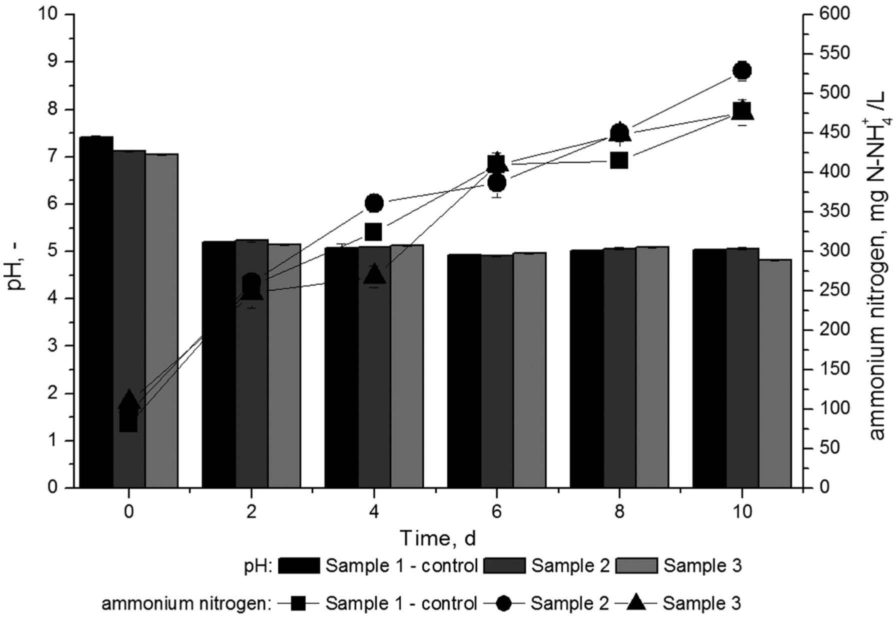

Figure 4. *Variations of pH and ammonium nitrogen during acid fermentation in second stage.*

in the concentrations of the tested indicators. There was no observed, that sonication of primary sludge affected significantly on the changes in the concentration of VFAs. During this stage, only few percent fluctuations in the value of VFAs concentration between the untreated and sonicated sludge were noted (Figure 3). Considering the entire fermentation period, the differences in concentrations of indicator were not more than 450 mg/L. Based to results second stage was found that volatile fatty acids are efficiently generated after the 4th day of the process. Similarly, changes in alkalinity, pH and concentration of ammonia nitrogen did not indicate that the sonication of substrates could lead to the significant intensification of transformations occurring during the acid fermentation. Fluctuations of concentrations of ammonia nitrogen, alkalinity and pH in all samples (3, 4, 5) during anaerobic digestion showed a similar tendency (Figures 3 and 4). Generally, up to 4 day of the process, increase alkalinity was observed. After the 4th day of fermentation alkalinity in all samples were stable and fluctuated around the level 1600 mg/L. For all samples rapid decrease in pH

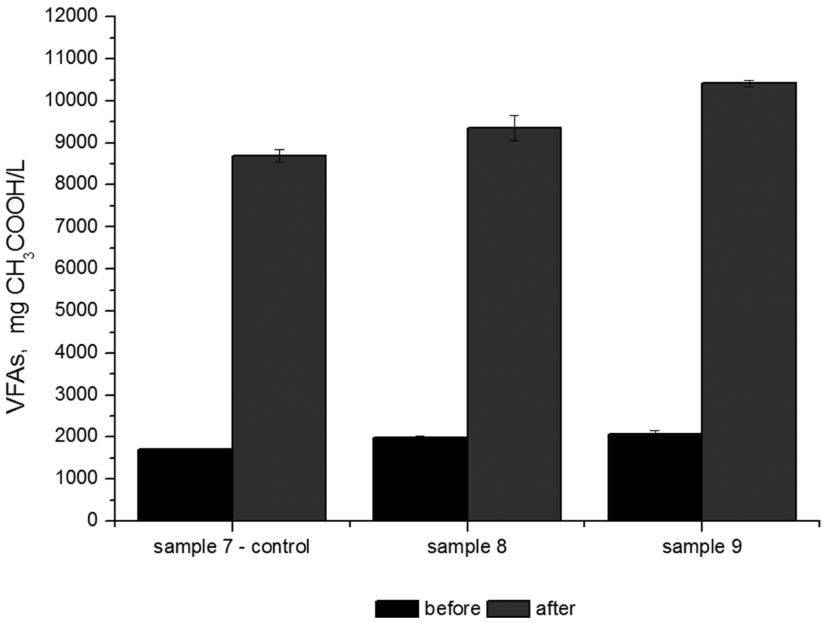

Figure 5. *Comparison of VFAs concentrations before and after 10 day fermentation.*

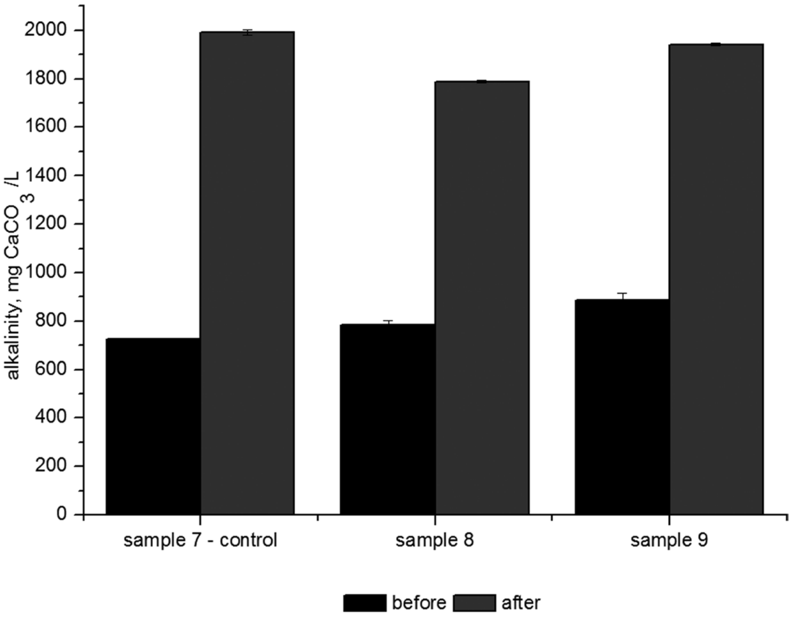

Figure 6. *Comparison of samples alkalinity before and after 10 day fermentation.*

was observed. On the second day of the process the pH achieved a local minimum (pH 5) and in the following days remained at this level (Figure 4). Changes in the concentration of ammonia nitrogen showed a linear upward trend. In the function of fermentation time the increase in N-NH$^+$ concentration from about 100 mg/L to 500 mg/L was observed (Figure 4).

3.3. Results of Stage III

The results of the investigated physicochemical parameters before and after the digestion process are presented in Figures 5–8. The results obtained in Stage 3 showed that sonication resulted in an increase VFAs generation by about 7% (sample 8) and 19% (sample 9), compared to an untreated sludge (sample 7). Results also showed that kind of inoculum had important impact on efficiency of the process. The highest VFAs generation was achieved for sample 9, wherein the inoculum was digested sludge from digester (Figure 5). While, the highest alkalinity was noted for control (sample 8) (Figure 6). The pH value showed an oppo-

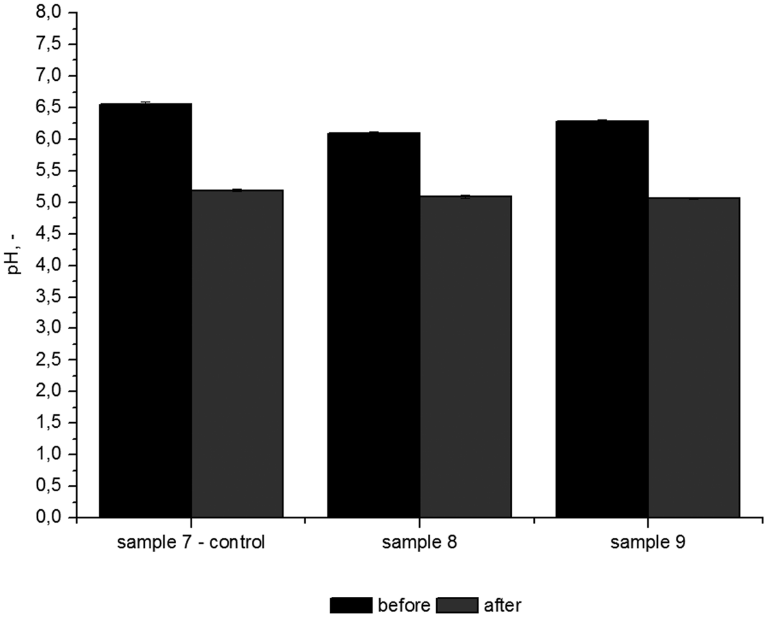

Figure 7. *The pH of samples before and after 10 day fermentation.*

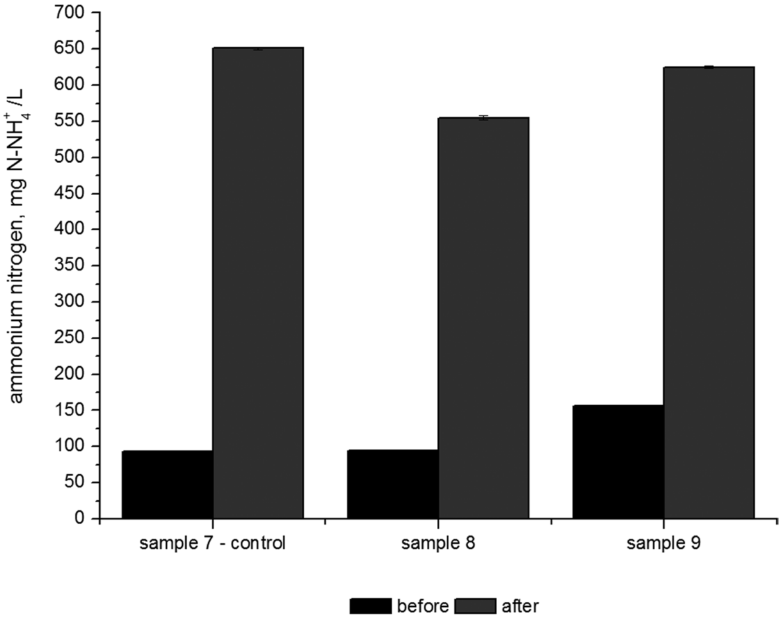

Figure 8. *Comparison of concentrations of ammonia nitrogen before and after 10 day fermentation.*

site tendency to the one noted for the VFAs concentrations. It was clear that the sonication of primary sludge resulted in a significant decrease of the pH (Figure 7). After the fermentation process, in all of the analyzed samples value of pH remained at 5. Based on obtained concentration of ammonia nitrogen, it found that the decomposition of organic matter was the most intense for the control and the sample 9 (Figure 8).

4. CONCLUSIONS

The aim of the study was to determine the possibility of intensification of acid fermentation of primary sludge as a result of sonication. The obtained results allow to concluding that such opportunities exist, although sonication of primary sludge requires considerable optimization.

It should be emphasized that the studies presented in article are cognitive tests. Research on acid fermentation of sonicated primary sludge will be continue taking into account the modifications based on the results of this experiment.

In studies applied low values of specific energy (lower than 5300.0 kJ/kg *TS*). This energy was lower than the recommended value for the disintegration of excess sludge prior to anaerobic stabilization. Probably it was a cause of small changes of studied parameters after pretreatment of sludge. Therefore, it is necessary to continue the experiments with higher doses of energy. The results achieved during experiments showed that propagation of ultrasonic wave of amplitude 61.0 µm was the most effective than amplitude 39.0 µm. It is suggested that the greater amplitude of the vibration allowed more extensive propagation of ultrasonic waves. This is particularly important in view of the high contents of dry matter in the tested samples. For this reason in future studies, optimization of content of dry matter in primary sludge is required This research should also include factors such as: nature of the inoculum and method of mixtures preparation and parameters of sonification (e.g. sample volume or sonication in dynamic conditions (sample mixing)).

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Optimizing Dilute-acid Hydrolysis (DACH) of Distillers Grains and Ethanol Fermentation

HAIWEI REN[1,2,*], FANGXIA PEI[2], JUNMEI XING[2], BINGYUN ZHANG[2], YI ZHANG[2], YONGGANG WANG[2],
ZHIZHONG LI[2], NA XU[2], TUO ZHAO[2] and XINGQUAN YAO[2]
[1]*Western China Energy & Environment Research Center, Lanzhou University of Technology, Lanzhou 730050, China*
[2]*School of Life Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, China*

ABSTRACT: Distillers grain (DG) is an abundant and low-cost lignocellulosic biomass. The objective of paper is to compare the influence of different acids on hydrolysis of DG and select the best acid. The results indicate that sulfuric acid is the most effective acid, and the optimum hydrolysis conditions are temperature 100°C, sulfuric acid concentration 2.0%, solid-liquid rate 1:12 (w/v), time 3.0 h. Under these conditions, the concentration of reducing sugar (RS) and xylose are 43.69 g/L and 35.16 g/L, respectively. The bioethanol production is around 11.82 g/L, which corresponds to 77.12% of theoretical yield and 0.14 g/g of consumed sugar.

INTRODUCTION

THE continuous depletion fossil fuel and increasing environmental concerns have triggered interest in alternative sources of bioenergy, such as bioethanol and biogas, *et al.* According to China government renewable energy law, bioenergy from renewable sources will account for 5% of primary energy by 2010 and 10% by 2020. Lignocellulosic biomass, such as relatively cheap, abundant, renewable agro-industrial by-products, which include high amounts of cellulose (35~50%), hemicelluloses (25~30%) and lignin (20~25%), are plentiful and potential fermentable sugars for bioethanol production.

The various processes involved during the conversion of lignocellulose biomass to bioethanol include pretreatment, saccharification hydrolysis, fermentation and separation [1]. Hydrolysis refers to the processes that convert the polysaccharides into monosaccharide, including of acid or enzymatic hydrolysis processes [2]. Enzymatic hydrolysis is uneconomical, although having characteristics of milder and more specific with higher bioethanol yields, requiring pretreatment to improve enzymatic digestibility. Acid can be used as catalysts for the hydrolysis as they breakdown heterocyclic ether bonds between sugar monomers in the polymeric chain. Moreover, acid-catalyzed hydrolysis is a quick easy and cost-effective reaction [3], which can be divided into two categories: concentrated or dilute acid hydrolysis. The use of concentrated acid may yield higher quantities of bioethanol, however, which have serious causticity to the equipments, leading to require reactors that are resistant to corrosion. Due to its ease of operation at both the experimental and industrial levels, the dilute acid is favorable way to hydrolyze lignocellulosic biomass [4,5]. Romero *et al.* studied the acid hydrolysis of olive tree pruning under different conditions of acid concentration and temperature [6]. Feng *et al.* studied the different dilute acids hydrolysis of *Enteromorpha* [7]. Xu *et al.* investigated the effects of hydrolysis conditions on the yield of pentose [8]. Akpinar *et al.* determined the effects of sulfuric acid concentration, temperature, and reaction time on the profile of reaction products [9]. Zhang *et al.* optimized of dilute acid-catalyzed hydrolysis of oil palm empty fruit bunch for high yield production of xylose [10]. Banerji *et al.* investigated the release of fermentable total sugar from sweet sorghum bagasse by dilute sulphuric acid hydrolysis [11].

China is a big country of white spirits production and consumption. In a typical distillation process, considerable amounts of distillers grains (DG) are produced, which are as the by-product in white spirits production. In China, the production of DG reached 50 million tons in 2013, and is expected to climb further in

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[*] Author to whom correspondence should be addressed.
E-mail: rhw52571119@163.com, Tel: +86 931 2976385

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the future. The vast majority of DG, contains of lignin, cellulose, hemicellulose, are disposed directly, which leads to huge waste of resources and solid waste polluting, except that only small amounts have been used as livestock feed, because of their high nutritional value, such as protein, polysaccharide, water-soluble vitamins and minerals. How to improve the value added of DG should be a question we must think currently. Many methods have been developed to find more effective ways for recycling this by-product, such as producing fermented feed, soy sauce, vinegar, activated carbon, organic fertilizer, microbial oils, ethanol and biodiesel. The bioconversion of bioethanol from DG, not only can make full use of DG, but also can resolve energy crisis and environment pollution.

In recent years, many efforts have been made to use DG as feedstock to produce bioethanol by the saccharification hydrolysis [12–15]. However, the research of different dilute acids hydrolysis of DG is rare. In this study, the objective of the work were to compare the hydrolysis efficiencies of different dilute acid (sulfuric acid, hydrochloric acid, acetic acid, nitric acid and maleic acid) to select the most effective acid, while producing significantly more fermentable sugars. Furthermore, the orthogonal design was used to optimize the dilute sulfuric acid hydrolysis. The potential bioethanol fermentability of produced sugar using *Saccharomyces cerevisiae* was studied. This work will be expected to form a new model of ecology, sustainable recycle development for traditional distillery.

MATERIALS AND METHOD

Raw Materials

DG was obtained from Jinghui liquor Corporation Limited in Gansu Province, China. It was dried at 105°C and milled to pass through a 1 mm screen. The particles was stored in plastic bag and sealed. The chemical compositions of DG are shown in Table 1.

Comparison of Different Dilute Acid Hydrolysis

DG (20 g, 18.04 g dry matter) was mixed with 240 mL of acid solution and the mixture was soaked for 24 h at ambient temperature. The DG was hydrolyzed with concentration of 2.0% (v/v) sulfuric acid, hydrochloric acid, acetic acid, nitric acid and maleic acid at temperature of 100°C, respectively. Once acid hydrolysis was completed, the residues were separated from liquid by centrifuge at 3000 r/min for 5 min. The residues were washed until the pH was 7.0 and further dried at 105°C. The supernatant was analyzed to determine the concentration of RS and xylose, the yield of xylose and RS were calculated as follows:

$$\text{Reducing sugar (RS) yield (\%)} = \frac{\begin{array}{c}\text{mass of reducing sugars in the}\\ \text{acid hydrolysate mass of biomass}\end{array}}{\text{mass of biomass}} \times 100\% \tag{1}$$

$$\text{Xylose yield (wt\%)} = \frac{\begin{array}{c}\text{mass of xylose in the}\\ \text{acid hydrolysate (g)}\end{array}}{\text{xylan mass of biomass}} \times 0.88 \times 100\% \tag{2}$$

Experimental Design for Dilute Sulfuric Acid Hydrolysis

The orthogonal design method L_9 (3^4) was used to optimize hydrolysis condition. The effect factors were temperature (A), sulfuric acid concentration (B), solid to liquid ratio (SLR, C) and hydrolysis time (D). Three levels were considered for each factor as showed in Table 2. The performance parameters considered were the concentration of RS (Y_1) and xylose (Y_2). Nine experiments with different combinations of factors and levels would be conducted.

Fermentation Experiment of Bioethanol

The optimal fermentation liquid obtained by acid hydrolysis was neutralized with sodium hydroxide, micropore film filtered successively, which was used for bioethanol fermentation. Bioethanol fermentation experiments were carried out as described by Li *et al.* [16]. After the fermentation, the RS and ethanol concentration in the supernatant was determined, according to the formula to calculate the yield of ethanol fermentation.

Table 1. Chemical Composition (dry-weight basis) of DG Used.

Component	Cellulose	Hemicelluloses	Lignin	Fat	Starch	Protein	Ash
Content (%,w/w)	32.08	20.23	9.93	3.56	13.59	16.94	6.23

Table 2. Factors and Its Levels of Orthogonal Design.

	A	B	C	D
Level	Temperature, °C	Sulfuric Acid Concentration, %, v/v	Solid to Liquid Ratio, g/mL	Hydrolysis Time, h
1	90	1.5	1:10	2.5
2	100	2.0	1:12	3.0
3	110	2.5	1:14	3.5

$$\text{Ethanol yield (wt\%)} = \frac{\text{mass of ethanol (g)}}{\text{mass of consumed reducing sugar}} \times 100\% \quad (3)$$

Analytical Methods

The analysis of cellulose, hemicelluloses and lignin were determined using Van Soest Fiber Analysis System. The concentration of RS and xylose were determined by the dinitrosalicylic acid (DNS) method and phloroglucinol colorimetry, respectively [17]. The content of ethanol was determined by potassium dichromate-DNS colorimetric. All analytical determinations were performed in duplicate and average data were reported.

RESULTS AND DISCUSSION

Comparison of Different Dilute Acid Hydrolysis Process

Acid hydrolysis was used to degradation the cellulose and hemicellulose polymers in DG to form fermentable sugars. The concentration of RS and xylose after different acids hydrolysis are shown in Figure 1. We compared the effects of sulfuric acid, hydrochloric acid, acetic acid, nitric acid and maleic acid on the hydrolysis process. In hydrolysis processes for five acids, RS and xylose increased initially with increasing treatment time. However, the RS and xylose concentration reached maximum plateau and sometimes even decreased at a long times, which means that longer time may not facilitate effective hydrolysis.The longer hydrolysis times might accelerate the degradation of polysaccharide, which lead to the loss of sugar yield caused by discharging soluble sugars from the samples. This argument was also supported by Nguyen *et al.* with the glucose formation of 120°C greater at 15min and decreased at 45 min of heating time which makes the maximum RS produce lower than 110°C [18].

Specifically, hydrochloric acid and sulfuric acid hydrolysis of DG were more effective and had the similar variation tendency in increasing the concentration of RS, the maximum concentration were 41.89 g/L of sulfuric acid and 42.78 g/L of hydrochloric acid, respectively. Moreover, hydrochloric acid is less effective than sulfuric acid, due to the RS/xylose yield of sulfuric acid reached a maximum when hydrolysis time was 3 h, in contrast, hydrochloric acid hydrolysis takes 3.5 h. Acetic acid is the least efficient, and the maximum RS and xylose concentration was less than the other acids. This is because of the fact that acetic acid provides the least hydrogen ion to the acid catalyzed hydrolysis.

From the RS and xylose yield point of view (Figure 2), the RS yield of sulfuric acid was highest when the time is 3 h, while hydrochloric acid was 4 h. As stated, the RS yield of sulfuric acid was more than that of hydrochloric acid, and xylose yield of hydrochloric acid was more than that of other acids. Thus, sulfuric acid is more efficient, because sulfuric acid has an extra hydrogen ion which creates more acidic medium to promote hydrolysis of the acid-sensitive 1,4-glycosidic linkages. As explained by Qian *et al.*, the hydrogen ion concentration is significant for RS release [19].

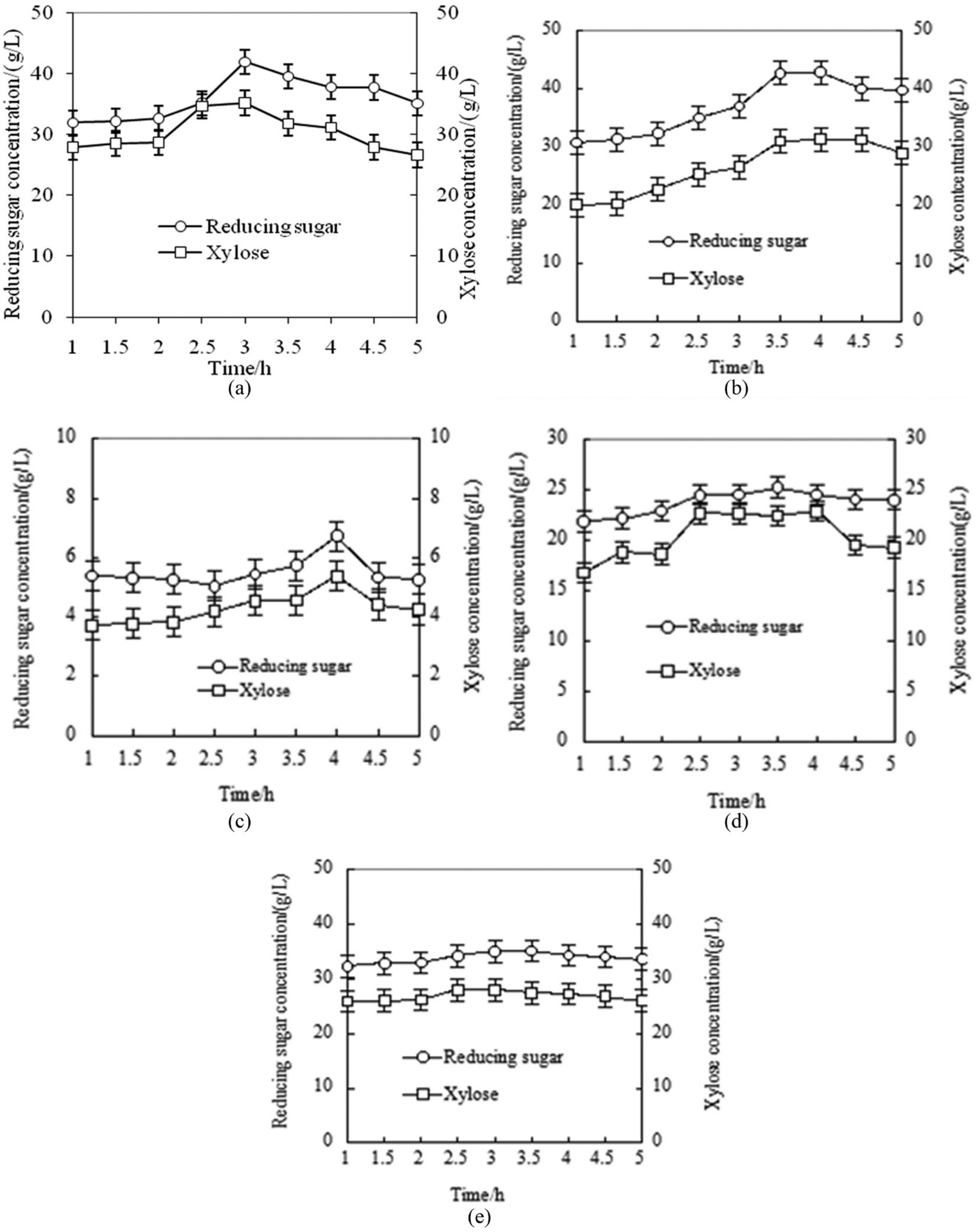
The hydrolysis of celllulose and hemicellulose may lead first to the monomeric sugars (xylose, glucose, *et al.*). However, acid hydrolysis may produce inhibitors, such as furfural and 5-hydroxymethylfurfural (HMF). Hydrolysis reactions are affected by the reaction time. If the sugars are the desirable end products of the hydrolysis, the appropriate acid hydrolysis can lead to higher yield of the RS.

Optimizing of Dilute Sulfuric Acid Hydrolysis Process

Kinetic studies carried out by Lenihan *et al.* show that substrate, acid concentration, temperature and reaction time can give effect to polysaccharide hydrolysis. Thus, several parameters were opimized to obtain maximum RS and xylose [20].

Effect of Hydrolysis Time on RS and Xylose Concentration

The release of RS/xylose from DG by sulfuric acid hydrolysis is shown in Figure 3(a). The concentration of RS/xylose was significantly influenced by hydrolysis time. The release of RS/xylose increased as the hydrolysis time increased, the maximum RS concentration obtained during the 3 h of hydrolysis time was 41.89 g/L, and the maximum xylose concentration obtained during the 3.5 h of hydrolysis time was 35.16 g/L, which were significantly higher than the other hydrolysis time. With the increase in hydrolysis time more than 4 h, both the concentration of RS/xylose decreased owing to degradation. The longer heating times might accelerate the degradation of polysaccharide, which lead to the 1oss of sugar yield caused by discharging soluble sugars from the samples. At



(a)

(b)

(c)

(d)

(e)

Figure 1. Reducing sugar and xylose concentration from DG after acid hydrolysis: (a) Sulfuric acid; (b) Hydrochloric acid; (c) Acetic acid; (d) Nitric acid and (e) Maleic acid.

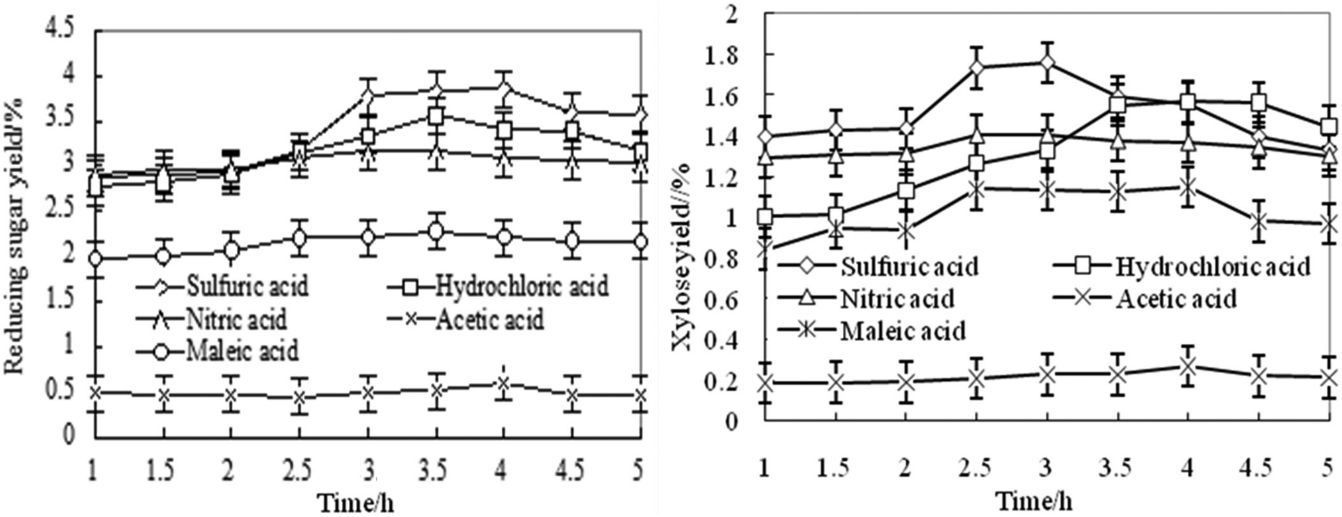


Figure 2. *Reducing sugar and xylose yield from DG after acid hydrolysis.*

early stage of reaction, the resistance crystalline structure and a lignin matrix form a physical barrier limiting its availability for acid hydrolysis. The hydrogen-bonds and the crystal structure were broken partly as the reaction progress, resulting in higher hydrolysis rate. However, the degradation of RS was increased, the recoveries of RS was decreased with the extension time. In particular, the concentration of RS and xylose was consistently increased with the hydrolysis time (2~3 h). This argument was also supported by Nguyen *et al.* with the glucose formation of 120°C greater at 15 min and decreased at 45 min of heating time which makes the maximum RS production lower than 110°C [18]. Hence, 3 h is chosen as ideal for further studies.

Effect of Temperature on RS and Xylose Concentration

The effect of temperature on the release of RS/xylose for 3 h is shown in Figure 3(b). When the temperature was less than 100°C has a positive effect on sugar yield. The amount of RS/xylose released increases from 26.2 to 41.89 g/L, and from 10.5 to 29.3 g/L, respectively. This means that temperature increase could enhance the productivity of the RS due to the increase in collision of the sulfuric acid between feedstock. The RS leveled off when the temperature varied from 100 to 120°C. According to Meinita, *et al.*, the heating temperature greater than 130°C with longer heating times can cause decomposition of RS to inhibitors [21]. This is also supported by Uppal *et al.* that high temperature with long heating times will reduce the formation of RS and produce more by-products [22]. This was because when temperature is raised to a certain level (90°C), part hydrogen bond fracture among DG lead to the structure becomes unstable. Once the crystalline structure of the cellulose is broke, acid molecules can access to the inner layers of the cellulose. In accordance with this theoretical model, a substantial amount of RS is formed at high temperature (90~100°C). More polysaccharide can be hydrolyzed to monosaccharide at a higher temperature. However, too high temperature leading to lower RS recoveries, due to a fraction of RS was degraded to inhibitors in acid and higher temperature conditions.

Effect of Acid Concentration on RS and Xylose Concentration

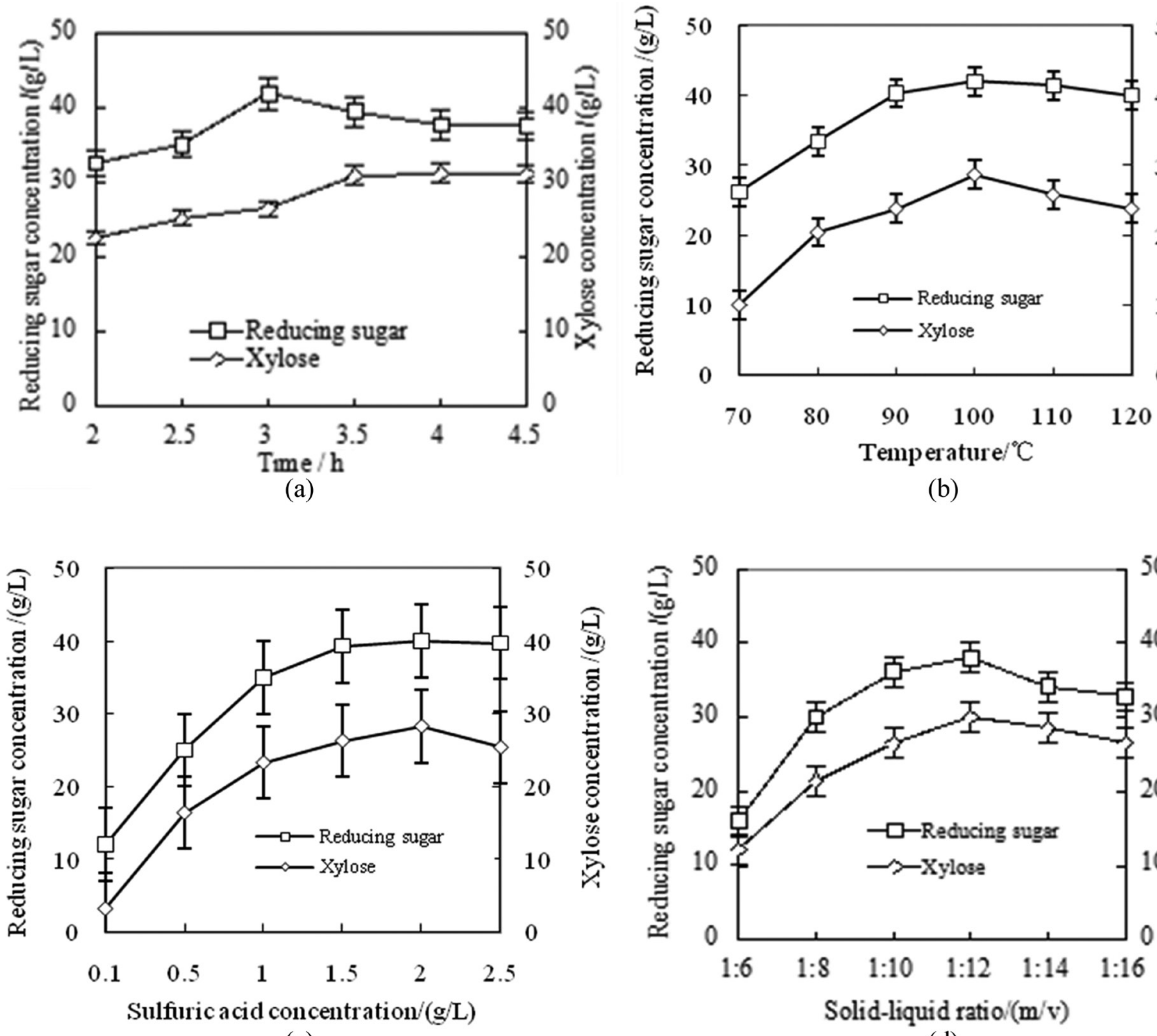
Figure 3(c) shows that the effect of the acid concentration on produce of RS/xylose. From these results, it was observed that an increase in acid concentration (until 2.0%) lead to a rapid increase of RS. During hydrolysis using 2.0% sulfuric acid, the RS and xylose concentration were 34.28 ± 0.976 g/L and 35.87 ± 3.610 g/L, respectively. At acid concentration of more than 2.0%, there are no significant increasing for both RS/xylose. One reason was that more hydrogen ions led to a higher degradation rate of hemicelluloses and cellulose, producing more RS and xylose. However, higher sulfuric acid concentration will cause the formation of inhibitors compounds (furfural and HMF), due to the increase in the activity of hydrogenions participating in the reaction as catalyst [23]. These results are in accordance with Meineta *et al.* [21]. As reported by Ge *et al.*, dilute acid can improve cellulose and hemicellulose conversion into monomeric sugars [24]. In addition, the application for lower acid concentration is better due to its low cost, less corrosive to equipment and avoidance from any environmental load. Hence, 2.0% of acid concentration was chosen for further studies.

Effect of the SLR on RS and Xylose Concentration

Figure 3(d) exhibited that the effect of different SLR on the release of RS/xylose. A similar pattern of the variation tendency for RS/xylose concentration was observed. The RS/xylose concentration started increasing sharply when the SLR decreased from 1:6 to 1:12. The highest RS/xylose concentration was obtained at SLR of 1:12, 38.2 and 30.5 g/L, respectively. Furthermore, the concentration of RS/xylose released decreased significantly with the decrease of sample loading. When heated with acids, cellulose and hemicellulose undergo hydrolysis to yield pentose or hexose such as glucose and xylose, which are the major ingredient of RS, dehydrating to form further. Once glucose is formed under reaction conditions, it can be degraded at a significant rate.

Optimization of Sulfuric Acid hydrolysis Process

For achieving higher RS/xylose concentration, the hydrolysis conditions were optimized through the L_9 (3^4) orthogonal design (Table 3). Four factors, namely temperature, sulfuric acid concentration, SLR, and hydrolysis time in three levels, were evaluated and optimized (Table 3). The K for each level of a factor was the average of three experimental. K_1~K_3 and k_1~k_3 were the RS and xylose concentration under the various investigated conditions, respectively. The maximum value was the optimum. In additition, according



(a) (b) (c) (d)

Figure 3. Effect of different factors on reducing sugars/xylose concentration: (a) Time; (b) Temperature; (c) Sulfuric acid concentration and (d) Solid-liquid ratio.

Table 3. L_9 $(3)^4$ Orthogonal Design and Experimental Results.

	A Temperature, °C	B Surfuric Acid Concentration, %,v/v	C Solid of Liquid Rate, g/mL	D Hydrolysis Time, h	Y_1 Reducing sugar concentration, g/mL	Y_2 Xylose concentration, g/L
1	1(90)	1(1.5)	1(1:10)	1(2.5)	37.24	14.82
2	1	2(2.0)	2(1:12)	2(3.0)	38.96	30.32
3	1	3(2.5)	3(1:14)	3(3.5)	39.29	30.77
4	2(100)	1	2	3	38.62	20.88
5	2	2	3	1	39.25	26.37
6	2	3	1	2	42.15	29.25
7	3(110)	1	3	2	42.79	30.37
8	3	2	1	3	38.07	10.32
9	3	3	2	1	37.96	15.48
K_1	38.5	39.55	39.15	38.15	the rank order of influential factors for Y_1: D > C > A > B	
K_2	40.01	38.76	38.15	41.30		
K_3	39.61	39.80	40.44	38.66	the optimum hydrolysis conditions: $A_2B_3C_3D_2$	
R	1.51	1.04	1.93	3.15		
k_1	25.30	22.02	18.13	18.89	the rank order of influential factors for Y_2: D > C > A > B	
k_2	25.50	22.34	22.23	29.98		
k_3	18.72	25.17	29.17	20.66	the optimum hydrolysis conditions: $A_2B_3C_3D_2$	
r	6.78	3.15	11.04	11.09		

to the largest donating rule, the factor with the largest range (K_{max}–K_{min} and k_{max}–k_{min}) has the greatest effect on the hydrolysis reaction. Table 3 shows that the rank order of the four influential factors are D > C > A > B for Y_1 and D > C > A > B for Y_2, respectively. Considering overall, the optimum hydrolysis conditions were $A_2B_3C_3D_2$ for both indexes, that is temperature of 100°C, sulfuric acid concentration of 2.5%, the SLR of 1:14 and hydrolysis time of 3.0 h.

Ethanol Fermentation of DG Hydrolysates

The DG hydrolysates were fermented using *S. cerevisiae* and the results are shown in Figure 4. According to the Figure 4, bioethanol production observed after 72 h of incubation was around 11.82 g/L, which corresponds to 77.12% of theoretical yield. The bioethanol production observed was 0.14/g of consumed sugar, which was inferior to 0.53 g/g and 0.61 g/g of liquid hot water and AFEX pretreated DG, respectively [25]. Velmurugan *et al.* reported the bioethanol production of about 0.43 g/g of glucose during the fermentation of hydrolyzed sugarcane bagasse [26]. The reason for lower bioethanol production was *S. cerevisiae* did not utilize pentoses released during acid hydrolysis. On the other hand, the degradation inhibitors of RS inhibit yeast cells and result in decreased bioethanol production rate. However, it was successful to fermentation DG hydrolysate to produce bioethanol.

CONCLUSION

It has been claimed that use dilute sulfuric acid hydrolysis of DG biomass was effective, since it possess extra hydrogen ion than the other acids. It means that, sulfuric acid was suitable to hydrolyse DG. The optimal sulfuric acid hydrolysis conditions were as follows: temperature of 100°C, sulfuric acid concentration of 2.0%, the SLR of 1:12 and hydrolysis time of 3.0 h. Under this optimal condition, the concentration of RS and xylose were 43.69 g/L and 35.16 g/L, respectively.

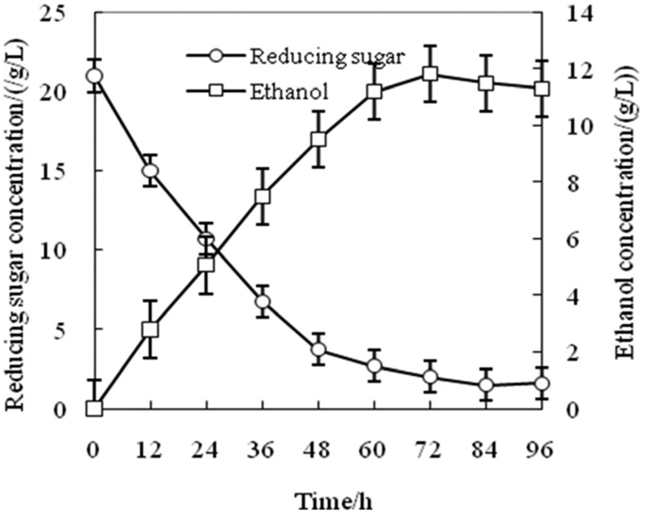


Figure 4. *Concentration profile of ethanol during fermentation of DG hydrolysate.*

To confirm the probability of DG hydrolysate for bioethanol production, fermentation was performed and ethanol production observed after 72 h of incubation was around 11.82 g/L, which corresponds to 77.12% of theoretical yield and 0.14 g/g of consumed sugar. It is feasible to produce bioethanol by fermenting saccharification liquid from DG, which not only reduce environmental pollution but also avoid the energy waste.

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Migration of Heavy Metal in a Sulfide Ore Tailings Impoundment

GUANG-HUA AI[1,2]*, YAN-FEI LIU[1], YONG WANG[3] and YULIN CHEN[4]
[1]*School of Resources and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou, China*
[2]*School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, China*
[3]*Hefei Testing and Quality Supervision Center for Geological and Mineral Products, The Ministry of Land and Resources, Hefei, China*
[4]*Institute of Geological Survey, Nuclear Industry Geological Bureau of Jiangxi Province, Nanchang, China*

ABSTRACT: Heavy metals are a component of sulfide ore tailings, which may pose serious threats to environment and human health. This study focuses on physical and chemical properties of main mineral composition in a sulfide ore tailings impoundment and discusses a series of chemical reaction equations of the main minerals in tailings including FeS, $Fe_{1-x}S$ and Fe_7S_8. This study aims to examine migration rules of the heavy metal elements in the tailings. To further investigate the migration mechanism, experimental simulation was used to provide some bases for the release and migration law of heavy metals in tailings.

INTRODUCTION

TAILINGS are from the flotation. The tailings were stacked in tailings pond nearby the mine. Since tailings granularity is small, especially the secondary mineral particles were very small, in weathering and oxidation conditions it was easy to react with air, water and biological components. Due to oxidation and leaching, acid water containing high concentration of heavy metals was produced. When the acid water flows into the vicinity of the water and the soil, it will further affect the whole ecosystem. The concentration of heavy metals in the tailing solution will be increased and significantly acidize with the weathering of sulfide minerals, leading to further activation, release and migration of heavy metals. This, hence, often poses serious threats to environment and human health. With fast social-economic development, such environmental issue has received increasing attention from the government and research institutions. In the literature, many studies have been conducted to reveal the sulfide oxidation and heavy metal leaching and migration in mining tailings. This paper analyzes the main components physical and chemical properties of tailings in the sulfide ore tailings pond, aiming to examine the migration law and secondary enrichment of heavy metal in tailings pond and the influence of leaching and plants on the heavy metals occurrence. Theoretically explore the mechanism of heavy metal migration to the surface environment in this paper.

MATERIALS AND METHODS

Collection and Characteristics of Tailing Samples

Sampling locations are located at the two vertical sections, one of which is parallel to the emission direction of tailings and the other of which is perpendicular to the emission direction. All samples from the two locations were collected using polyethylene plastic bags. The sulfide ore tailings, such as pyrite, magnetic pyrite, white iron ore, glue pyrite, exit in the system as the monomer form. Adhesive tailings adjoin gangue, and fine grains of pyrite mine are often covered within or adjoin the gangue. Coarse grains of galena, marmatite, sphalerite often adjoins pyrite mine or gangue, and fine grains of them are monomers [1]. Copper mineral, arsenopyrite would adjoin or be covered by pyrite mine. There would be few grains of cassiterite in the tailings, which would be covered by pyrite mine or adjoin gangue. Analysis of major elements in tailings is shown in Table 1.

Analyzing Method

The tailing samples were dried in oven at the temperature of 40°C, and ground into 100 meshes. The contents of Cu, Pb, Zn and Cd were analyzed through atomic absorption spectrometry and chemical analyz-

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*Author to whom correspondence should be addressed.
E-mail: guanghua_ai@126.com, Tel: 13970781484

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Table 1. Major Element in Tailings.

Element	Cu	Zn	Pb	S	As	Cd	Sn	Fe	SiO_2	CaO	MgO	Al_2O_3
Content (%)	0.08	0.62	0.37	15.78	0.50	0.02	0.11	20.07	12.62	15.69	7.69	2.58

ing methods. Each grounded sample was treated according to the procedure described as follows. Put 0.1 g of a sample into polytetrafluoroethylene plastic crucible. The sample was then combined with 5 ml HNO_3, 10 ml HF, and 12 ml $HClO_4$ and heated at a low temperature until the white smoke disperses. After cooling, it was added with 10 ml 1:1(V/V) HCl. After its dissolution at low heat, it was transferred into a 50 ml measuring flask for further analysis. The following instruments were used for analyzing the sample: PS-6 vacuum inductively coupled plasma atomic emission spectrometry (ICP-AES) made by American Baird Company. Test conditions: Rf generator frequency: 40.68 MHz, power 1100 W. Cooling gas: 10 $L \cdot min^{-1}$; Carrier gas: 0.3 $L \cdot min^{-1}$, Plasma gas: 0.4 $L \cdot min^{-1}$. The integration time is 5 seconds and the number of integral times is three.

The test method for heavy metals chemical speciation is described as follow: HNO_3–$HClO_4$–HF digestion and plasma atomic emission spectrometry (ICP-AES) test would be adopted to commit gross analysis of mineral elements and heavy metal elements. Three successive extraction methods was adopted to classify the heavy metal elements, which can be divided into 4 kinds of components including acid extractable state, oxide combination state, organic combination state and residual state.

RESULTS AND DISCUSSION

Environmental Geochemistry Characteristics

Examining the migration rule of heavy metals is the most concerning aspect of the study on heavy metals pollution in nonferrous metal mining. Due to many factors, e.g., weathering and oxidation, the toxic heavy metals in tailing could eventually release and migrate through the tailings wastewater, resulting in serious environmental pollution. Therefore, comprehensive understanding of the physical and chemical characteristics of tailings mineral is of great significance [2]. Most primary tailing minerals turn to be inert during the weathering process, such as quartz and most of the silicate minerals. Oxidation of sulfide is the major mechanism of acid production and release of heavy metals. Acid production is related to the oxidation of pyrite and pyrrhotite. In other words, physical and chemical changes including weathering and oxidation of the toxic heavy metals in tailings are primarily due to physical and chemical reactions between sulfide minerals in tailings with soil, air and water. Therefore, to study the migration rule of heavy metal in tailings, understanding physical and chemical properties of sulfide mineral is the first step.

According to the type of compound, sulfide mineral belongs to the ion compounds. Examination of physical properties shows that it has obvious difference from typical ion lattice crystal. This is primarily due to the fact that sulfide mineral displays obvious covalent bond, and others display metallic bond. The complexity of the chemical bonds of sulfide mineral is decided by the special electronic structure of atoms in sulfide mineral. As each sulfide mineral has certain a chemical composition, the atoms, molecules or ions in the mineral would remain balance through the action of the chemical bonds. When exposed to air, water and various liquids, sulfide mineral would have a series of different chemical changes such as oxidation, decompose and hydrolysis. Because different kinds of sulfide minerals have various chemical compositions and bonds, associated chemical properties are also different. Oxidation, dissolubility and various acid and alkaline reactions of sulfide mineral have close relationship with the release of the heavy metals in tailings.

The sulfide mineral is difficult to dissolve in water. However, in acid aqueous and oxidation conditions, its solubility will increase significantly. Under these conditions soluble sulfate could be produced and this makes the liquid acidic, which could accelerate the dissolution of the mineral. Due to the acid rain and acid yield potential of sulfide minerals, tailings are often in acid liquid, which speed up the dissolution of sulfide mineral in tailings. Dissolved in the water and being released with the acid wastewater drainage of the mine, heavy metals could migrate to supergene environment and pollute ecological system of the mining area.

When the sulfide minerals, especially the minerals which contain elements with electrovalence change (such as Fe, S, etc), are exposed to the surface of earth, its reactions with oxygen in air and dissolved oxygen, carbon dioxide and water make the original ions turn into oxidation state. For instance, Fe^{2+} could be turned into Fe^3 and S^{2-} or $[S_2]^{2-}$ could be turned into S^{6+}. This leads to the destruction of the original mineral and form some stable minerals in oxidation environment. e.g., low oxide could be turned into high oxide or hydrogen chloride; sulfide could be turned into sulfate. When oxidation process is not complete, the surface characteristics would be changed. All the reactions that make the mineral oxidized and its characteristic changed are called as mineral oxygen [3].

Oxygenizement of pyrite is as follows:

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$

$$12FeSO_4 + 3O_2 + 6H_2O = 4Fe_2(SO_4)_3 + 4Fe(OH)_3$$

$$4FeSO_4 + O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O$$

$$Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4$$

Oxygenizements of covellite and copper pyrites are as follows:

$$CuS + 2O_2 = CuSO_4$$

$$CuFeS_2 + 4O_2 = CuSO_4 + FeSO_4$$

Oxygenizement of chalcocite is as follows:

$$2Cu_2S + 5O_2 + 2H_2O = 2CuSO_4 + 2Cu(OH)_2$$

$$4Cu_2S + O_2 = 4CuS + 2Cu_2O$$

$$Cu_2S + 2O_2 = CuSO_4 + Cu$$

$$4Cu_2S + 9O_2 = 4CuSO_4 + 2Cu_2O$$

Oxygenizement of bornite is as follows:

$$2Cu_5FeS_4 + 17O_2 = 6CuSO_4 + 2FeSO_4 + 2Cu_2O$$

In the condition of ferric sulfate, oxygenizements of pyrite, covellite, copper pyrites, chalcocite and bornite are as follows:

$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S^0$$

$$CuFeS_2 + 2Fe_2(SO_4)_3 = CuSO_4 + 5FeSO_4 + 2S^0$$

$$CuFeS_2 + 2Fe_2(SO_4)_3 + 3O_2 + 2H_2O = \\ CuSO_4 + 5FeSO_4 + 2H_2SO_4$$

$$Cu_2S + Fe_2(SO_4)_3 = CuS + 2FeSO_4 + CuSO_4$$

$$Cu_2S + 2Fe_2(SO_4)_3 = S^0 + 4FeSO_4 + 2CuSO_4$$

$$Cu_5FeS + 6Fe_2(SO_4)_3 = 5CuSO_4 + 13FeSO_4 + S^0$$

In addition, the oxidation of sulfide minerals is closely related to their thermodynamic properties. The oxidation process also is sensitive to the environment parameters such as temperature, humidity, pH value and Eh value. Therefore, in determining the directions of sulfide mineral oxidation reaction process, one should know about important parameters including molar volume, standard entropy, standard formation free energy of sulfide mineral, and should take full advantage of the environmental conditions of the tailing pond.

Migration Mechanism of Heavy Metal in Tailings

Major mineral components in the tailings are shown in Table 1. The content of pyrite is relatively high, and that of galenite and sphalerite are quite low. Large amount of iron sulfide in the tailings could be oxidized and a certain amount of acid could be released during this process, which could acidize the wastewater and pore water. Acidized wastewater and pore water could further speed up the further acidification of sulfide mineral, resulting in higher heavy metal concentration in the tailings.

In general, the mechanism of oxidation and weathering of sulfide mineral and other major mineral in tailings could be shown in the following expressions:

$$Fe_{1-x}S + (2 - x/2)O_2 + xH_2O \rightarrow \\ (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+$$

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$CuFeS_2 + 4O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-}$$

$$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}$$

$$PbS + 2O_2 \rightarrow PbSO_4$$

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + 2H_2O$$

$$MgCa(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$$

$$MgCa(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O$$

$$K(Mg, Fe)_3AlSi_3O_{10}(OH)_2 + 7H^+ \rightarrow \\ K^+ + 3(Mg, Fe^{2+}) + Al(OH)_3 + 3SiO_2 + 3H_2O$$

If the oxidation process is not complete, S could be generated through the following equation.

$$2Fe_{1-x}S + (1-x)O_2 + (4-4x)H^+ \rightarrow \\ (2-2x)Fe^{2+} + 2S + (2-2x)H_2O$$

Iron ion could also be used as the oxidizer of iron pyrites and pyrrhotite, as shown in the following equations:

$$2\mathrm{FeS_2} + 14\mathrm{Fe}^{3+} + 8\mathrm{H_2O} \rightarrow 15\mathrm{Fe}^{2+} + 2\mathrm{SO_4^{2-}} + 16\mathrm{H}^+$$

$$\mathrm{Fe}_{1-x}\mathrm{S(s)} + (8-2x)\mathrm{Fe}^{3+} + 4\mathrm{H_2O} \rightarrow (9-3x)\mathrm{Fe}^{2+} + \mathrm{SO_4^{2-}} + 8\mathrm{H}^+$$

$$\mathrm{PbS} + 2\mathrm{Fe}^{3+} + 3\mathrm{SO_4^{2-}} + 3/2\mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{PbSO_4} + 2\mathrm{Fe}^{2+} + 3\mathrm{SO_4^{2-}} + 2\mathrm{H}^+$$

$$\mathrm{Fe}_{1-x}\mathrm{S(s)} + (2-2x)\mathrm{Fe}^{3+} \rightarrow (3-3x)\mathrm{Fe}^{2+} + \mathrm{S}^0\mathrm{(s)}$$

Tailing is the complicated heterogeneous artificial hybrid debris. Its mineralogical characteristics are closely related to ore types of minerals, sulfide ore content, buffer capacity and regional climate (temperature, rainfall). Researching on tailing mineralogy is important for solving tailing pollution, because all changes and environmental hazards in tailing result from the complex water-gas-mineral reaction under special conditions. Many minerals are sensitive to environmental conditions, especially the temperature, humidity, pH value and Eh value. Water-air-mineral reaction causes the decomposition and transform of original minerals and the formation of new minerals. Oxidation, neutralization, sorption, ion exchange of tailing would control the process of the acid drainage and release of heavy metal. Therefore, with complete understanding of the chemical reaction and transform occur in tailing and comprehensive knowledge of mineralogy and mineral combination, one may possibly predict the toxicity and environmental dangers of heavy metal in tailing.

From the above chemical reaction processes, we can see that the oxidation of sulfides releases a certain amount of H^+, Fe^{x+}, $\mathrm{SO_4^{2-}}$ and other metal ions into the pore water of tailings. At the same time, the acid liquid would accelerate oxidation and dissolution of sulfide and other rock forming minerals. Therefore, more elements from tailings would be released. In fact, not all of the minerals would be involved in oxidation. Complex factors such as humidity, structure and size of the mineral and depth, mineral form, $\mathrm{O_2}$, pH and organic substances would influence the mineral oxidation in the tailing. The oxidation of sulfide releases a certain amount of H^+, Fe^{x+}, and $\mathrm{SO_4^{2-}}$. This is the first step of the migration of metal elements into the environment. The migration is further influenced by a series of complex reactions such as precipitation hydrolysis reactions, ion exchange and adsorption/desorption. Neutralization, adsorption/desorption, precipitation, and ion exchange are all important mechanisms which may lead to the migration of heavy metals in mines.

In mine environment, however, the migration of various heavy metals could change with the chemical properties of solid mineral and liquid. Thus their migration mechanisms are not unique, and even the migration rules of a kind of metal would differ spatially and temporally [4]. Besides the theoretical study on migration rule of heavy metal ion in tailing, researchers also try to prove the phenomenon of ion release in tailing by testing ion concentration of water and soil in surrounding environment.

Through previous studies on oxidation reaction mechanism of major sulfide mineral in tailing, it is reasonable to assume that the oxidation reaction would release a certain amount of H^+, Fe^{x+}, $\mathrm{SO_4^{2-}}$, which is the first step of the migration of metal elements into the environment. In other words, acidification potential makes the leakage of tailing acidized constantly, and acidized leakage accelerates the migration of heavy metal ions in tailing to surrounding environment [5].

Experimental Simulation of Release Disciplines of Heavy Metal Ion

Migration of heavy metals can be verified through tests of ion concentrations in surrounding water and the soil nearby the tailing pond. At the same time, many studies used experimental simulation to investigate the release and migration mechanism of heavy metals under wastewater or rain eluviation conditions. It is well accepted that the dissolution is a long process. Thus sulfide ore tailings are a continuing pollution source of heavy metal ions to the environment.

Influence of pH on Heavy Metal Migration

The sulfide ores were eluviated with the solution of pH 2 ~ 7 for 50 days. The result shows that acidity can significantly increase the dissolution of heavy metals (Pb, Zn, Cu and Cd) in tailing ores. Under different conditions (pH = 2, 4, 6 and 7), the results of eluviate are obviously different, the difference upon Cu is the most remarkable. At room temperature, use leaching solutions of different pH value to dissolve tailings for 50 days, the mass concentration of Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} would be tested.

Experimental data were further analyzed to further our understanding. First, all the 500 ml used leaching solutions were collected every day. The total dissolu-

Table 2. Dissolution of Heavy Metal in Different pH Value Leaching Solutions.

Element	pH = 2	pH = 4	pH = 6	pH = 7	Standard Deviation	Variation, %
Pb	9.41	7.54	5.24	3.88	2.47	38.42
Zn	410.21	342.5	282.3	232.6	75.68	24.55
Cu	1.82	1.05	0.82	0.46	0.55	56.31
Cd	0.45	0.36	0.35	0.32	0.068	19.66

tion volume of heavy metal in different pH value solutions was calculated according to the concentration of heavy metal every 24 hours, as shown in Table 2. From the table, we find that variation of total dissolution volume of Cu in different leaching solutions is the largest, followed by Pb, Zn and Cd. Therefore, sensitive degrees of the four metals are Cu, Pb, Zn and Cd in descending order.

According to concentration of Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} in 50 days leaching solutions, the following figures (Figures 1 to 4) could be drawn.

From the above diagrams, it is found that the pH value of the leaching solution influences the release of Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+}. When the pH value is less than 7, the ion concentration of tailing rises rapidly with the decrease of pH value. When the solution pH value is close to 7, the ion concentration of tailing changes slightly with the change of pH value. In the 50-day leaching experiment, except Zn^{2+}, the concentrations of Pb^{2+}, Cu^{2+} and Cd^{2+} decreased with the increasing leaching time. As for Zn^{2+}, when the leaching solution is a weak acid or base, the leaching time has almost no influence upon the dissolution. When the leaching solution is a strong acid, the concentration of the leaching solution increases rapidly after leaching for 30 days, as shown in Figure 3. Therefore, the acidification of tailing provides a key condition for the release of heavy metal ions. In China, acid rain is a very serious concern, especially in the southern part. Sulfide minerals have the acidizing potential. These two actions will speed up the dissolution of heavy metal ions such as lead and zinc in sulfide ore tailings, resulting in serious conditions of heavy metal pollution. Therefore, controlling of acidification of the tailings is critical to reduce the hazard from heavy metal [6].

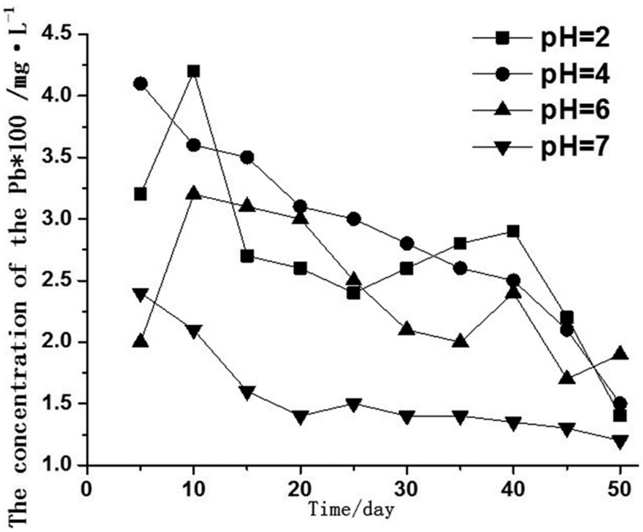

Figure 1. *The concentration of the Pb under different pH conditions.*

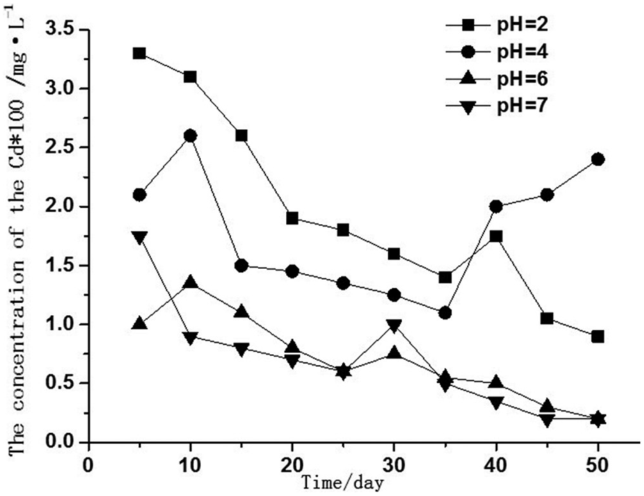

Figure 2. *The concentration of the Cd under different pH conditions.*

Conductivity Variation in the Immersion Liquid

Dissolutions of the every-5-days experiment were taken for EC evaluation. The results are shown in Figure 5. When pH value is less than 4, the solution con-

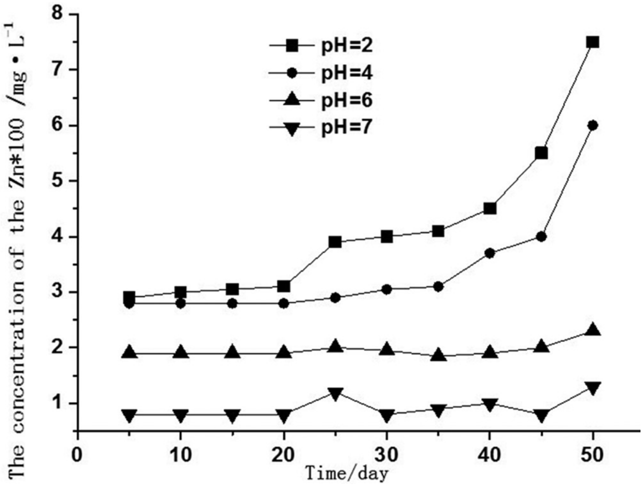

Figure 3. *The concentration of the Zn under different pH conditions.*

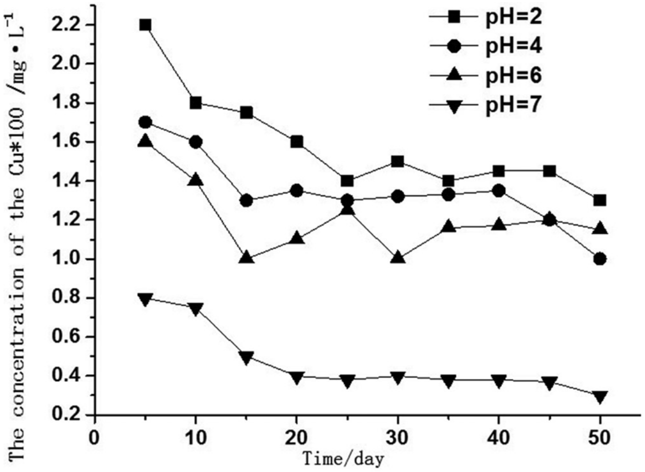

Figure 4. *The concentration of the Cu under different pH conditions.*

ductivity of leaching solutions increases significantly after 30 days leaching. When the leaching solution is in a weak acidity or weak alkali condition after 50 days leaching, there was little variation between 0.5~1.5 ds·m^{-1}. The results show that the pH value of leaching solution has direct connection with conductivity. In acid conditions, it can enhance the dissolution of solid material and increase the content of salt in tailing.

With the increase of leaching time, the concentrations of Pb, Cd and Cu in various leaching solutions reduce gradually. While the concentrations of Zn increase, and the lower the pH value of leaching solution and the longer the leaching time was, the more obvious of the rising trend could be. The leaching experiment was compared to the dissolve experiment. It is found that during the same time span, the total dissolved volume of metals in former experiment is 3 orders of magnitude higher than the latter one.

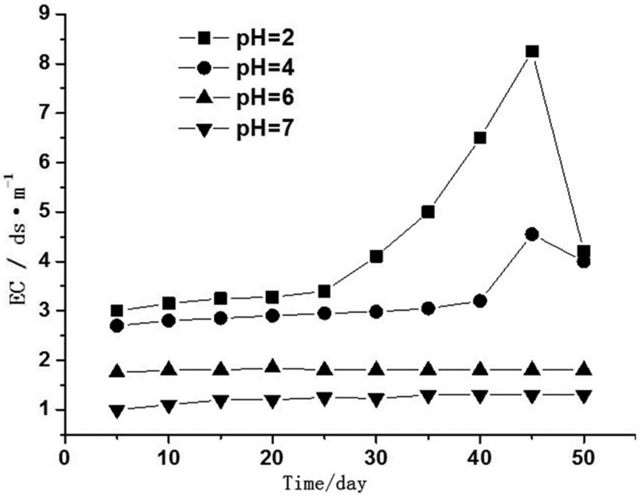

Figure 5. *Conductivity varying with time in the immersion liquid of tailings.*

Therefore, experimental simulation of release disciplines of heavy metal ion proves the analysis of release and migration theory in this study. No matter in wastewater, soaking in tailings, or in leaching rain, heavy metals would be released constantly from tailings and migrated with wastewater to its surrounding environment, especially in the southern acid rain and hot summer weather.

CONCLUSION

Heavy metals, potentially causing serious threats to the environment and human health, could be released through migration in tailings. This study focuses on the migration mechanism of heavy metals in tailings. Through analysis of physical and chemical properties of main mineral composition of tailings and discussions of a series of chemical reaction equation for the main minerals in tailings, including FeS, $Fe_{1-x}S$ and Fe_7S_8, the migration mechanism of heavy metals were discussed. The reaction occurring in the tailings lead to release of H^+, Fe^{x+}, SO_4^{2-} and other metal ion into pore water. The released acid solution could fasten oxidation and dissolution rate of sulfide and other mineral of tailings. Therefore, more heavy metal elements could be released from tailings. This is the key to the release and migration of heavy metal elements. Further migration of heavy metal elements is controlled by a series complex of precipitation and hydrolysis, ion exchange and adsorption, desorption. Therefore, neutralization reaction, adsorption, desorption, precipitation and ion exchange are the important reason to the migration of heavy metals. Experimental simulation discussed in this paper proved some bases for the release and migration law of the heavy metals elements in tailings.

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A Research on the Leaching Toxicity of the Solid Waste of a Pb-Zn Mine

SHUN-CAI WANG[1,*], ZHI-CHENG WEI[1], YAN ZHOU[1] and FANG-HAN WANG[2]
[1]*Key Laboratory of Integrated Regulation and Resource Development on Shallow Lake of Ministry of Education,*
College of Environment, Hohai University, Nanjing 210098, China
[2]*Nanjing YinMao Lead-Zinc Mine Co. Ltd, 89# Xixia Street, Nanjing 210033, China*

ABSTRACT: Mine activities may cause serious environmental problems. Whether the solid wastes from the mine pollute the environment is the one of the problems. The solid wastes from the Nanjing YinMao Lead-Zinc Mine were investigated by multiple mineralogical techniques in this paper. Calcite and quartz were the major components of the solid wastes by X-ray diffraction spectrum. Several elements such as O, Mg, Zn, Fe, Mn, Ca, K, S, Si, Al, As and Na were detected in the solid wastes by electron microprobe analysis. Although the solid wastes contained heavy metals, their concentrations in the leaching solution of the solid wastes by ICP were less than the identification standard for hazardous waste. Therefore, the solid wastes from the Nanjing YinMao Lead-Zinc Mine are not hazardous.

INTRODUCTION

MINE activities may cause serious environmental problems. The weathering of mine solid wastes may produce acid mine drainage (AMD) [1–3]. Lots of metal ions dissolve in acid mine drainage. The discharge of the acid mine drainage seriously contaminates the soils, ground water and surface water [4–6]. The mechanisms of acid mine drainage are that mine solid wastes react with oxygen and water from the atmosphere [7,8]. Whether the solid wastes from the mine release heavy metal ions under acid conditions, the contents of heavy metal ions in the leaching solutions exceed the national standard for hazardous waste identification is worth studying.

The Nanjing YinMao Lead-Zinc Mine was founded in 1957. Every year, the Nanjing YinMao Lead-Zinc Mine releases about 48000 t waste rocks from the underground stope, releases about 90000 t tailings and 800t sludge from the mineral processing plant. For this paper, X-ray diffraction spectra (XRD) were used to test the mineral compositions in the waste rocks, tailings, sludge and solidified solid waste, the contents of elements in the waste rocks, tailings, sludge and solidified solid waste were tested by electron microprobe analysis (EMPA), the extraction toxicity using inductive coupled plasma emission spectrometer (ICP) was studied to evaluate the quality of them.

MATERIALS AND METHODS

Background of the Nanjing YinMao Lead-Zinc Mine

The Nanjing YinMao Lead-Zinc Mine, which is situated in the eastern suburb of Nanjing City, is the largest nonferrous metals mine in eastern China. The ore deposits, which appear as saccular, lenticular and stratiform forms, mainly contain pyrite, sphalerite, rhodochrosite, chalcopyrite, tetrahedrite, galena, and marcasite ore minerals. The most important ore body is 23 m thick and 850 m long on average.

The Nanjing YinMao Lead-Zinc Mine employs a method so-called upward horizontal layered mining and backfilling in underground stope. Both waste rocks from the underground stope and tailings from the mineral processing plant are used to backfill the stope. The underground stope releases about 100 t waste rocks and the mineral processing plant releases about 300 t tailings everyday [9]. It is important and urgent to determine whether the waste rocks and tailings release heavy metals, due to the high contents of heavy metals in these solid wastes.

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*Author to whom correspondence should be addressed.
E-mail: wshcai@hhu.edu.cn

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Samples and Analytical Instruments

The waste rocks samples collected from the Stope of 475 m underground in the Nanjing YinMao Lead-Zinc Mine were milled into powder for XRD, EMPA and leaching toxicity analysis. The tailings, sludge and solidified waste samples were collected from the mineral processing plant in the Nanjing YinMao Lead-Zinc Mine. These samples were air-dried for XRD, EMPA and leaching toxicity analysis. A Bede D/MAX-3A diffractometer was used to collect the XRD spectra. JEOL JXA-8100 was used to electron microprobe analysis.

Leaching Method

Extraction reagent used in this paper was adjusted with 2d mixture and 1L water. The pH of the extraction reagent is about 3.20. The mixture was formed with 1 g HNO_3 and 2g H_2SO_4. 2L extract vessels with 1500 mL extraction reagent and 150 g of each sample were shaken at a temperature of 23 ± 2°C with a speed of 30 ± 2 rpm in a horizontal shaking mixer for 18 h. Through a 0.8 µm-lmpore glass fiber filter paper, the leaching solution in each vessel by using vacuum-filtration was separated from the solid phase at the end of the extraction. The concentrations of toxic elements in the leaching solution were tested by inductive coupled plasma emission spectrometer (ICP).

RESULTS AND DISCUSSION

Mineralogy of the Solid Waste from Nanjing YinMao Lead-Zinc Mine

The Nanjing YinMao Lead-Zinc Mine exploits the underground mineral resources through blasting. The large rocks were crushed to small rocks, whose particle diameters were less than 30 cm. The small rocks rich in pyrite, sphalerite, rhodochrosite, chalcopyrite, tetrahedrite, galena, marcasite ore minerals were sent to the mineral processing plant, the rest were called waste rocks, and were left in the underground stope. Waste rocks may produce acid mine drainage (AMD). AMD contains high concentrations of dissolved metals. The discharge of the AMD may contaminate the soils, ground water and surface water. The mechanisms of acid mine drainage are that sulfide minerals react with oxygen and water from the atmosphere, and thereby cause release of acidic, metal-laden leaching solution. Whether the waste rocks from the mine contain sulfide minerals is worth testing.

On the basis of the XRD analysis, calcite and quartz were mainly ore minerals in the waste rocks from the Nanjing YinMao Lead-Zinc Mine. (Figure 1), sulfide minerals were not identified from the XRD spectrum of the waste rocks. This shows that the waste rocks from the Nanjing YinMao Lead-Zinc Mine not have the possibility of producing acid mine drainage.

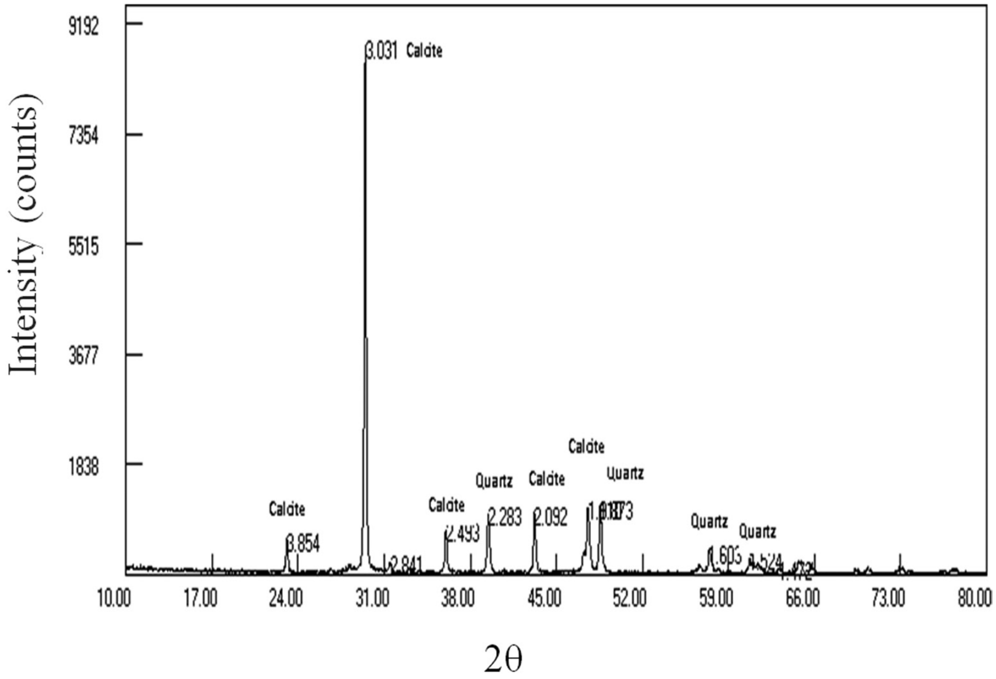

Figure 1. *XRD spectrum of the waste rocks from the Nanjing YinMao Lead-Zinc Mine.*

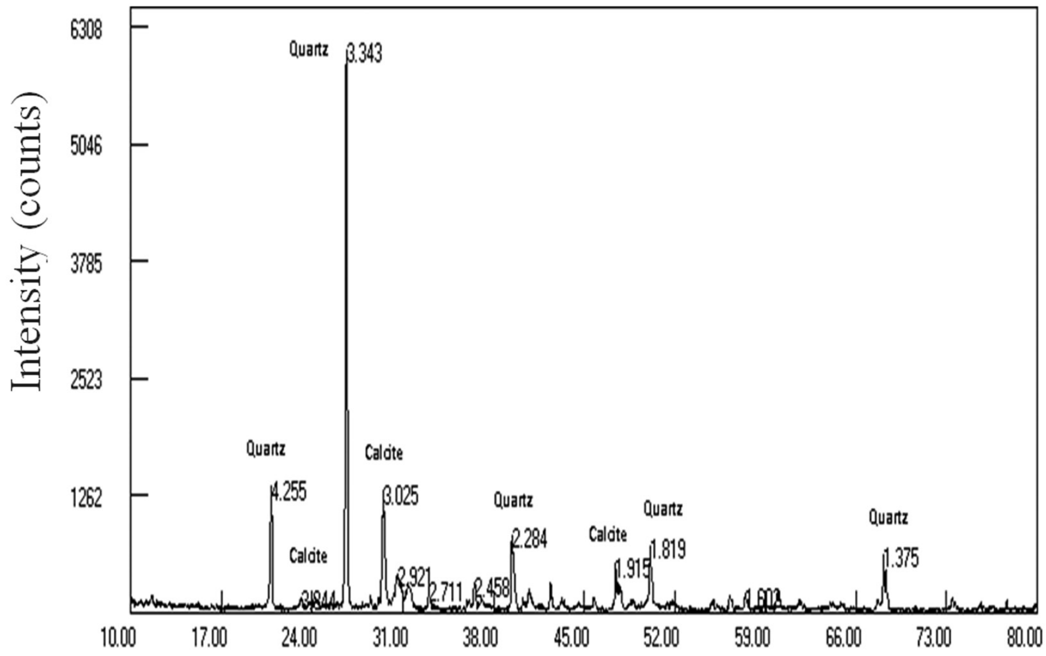

Figure 2. *XRD spectrum of the tailings from the Nanjing YinMao Lead-Zinc Mine.*

The small rocks rich in pyrite, sphalerite, rhodochrosite, chalcopyrite, tetrahedrite, galena, marcasite ore minerals, which were sent to the mineral processing plant from the underground stope, were milled into pulp by crushers and ball mills. The percent of the particles, whose particle diameters were less than 0.074 mm, were more than 80% of all the particles in the pulp. The concentration of the pulp was 30%. Lead, Zinc, Sulphur and Manganese ore concentrates were obtained respectively from the pulp by selective flotation, the rest were called tailings. Whether the tailings from the mineral processing plant of the Nanjing YinMao Lead-Zinc Mine contain sulfide minerals is worth testing.

On the basis of the XRD analysis, calcite and quartz were mainly ore minerals in the tailings from the Nanjing YinMao Lead-Zinc Mine. (Figure 2), sulfide minerals were not identified from the XRD spectrum of the tailings. This shows that the tailings from the Nanjing YinMao Lead-Zinc Mine not have the possibility of producing acid mine drainage.

The mine water discharged from the mineral processing plants of the Nanjing YinMao Lead-Zinc Mine is treated by means of coagulation with sodium carbonate and alum which are fed into the mine water pipelines. Intensive stirring occurs in the pipeline and the well below the settling tank. The water is then discharged to the settling tanks where the suspended matters in the water undergo coagulation and sedimentation. The application of sodium carbonate and alum in the process of mine water treatment generates significant quantities of suspension that is difficult to sediment. To shorten the clarification time of treated water, polyacrylamide was applied. After the completion of a working cycle, the accumulated sludge is removed from the settling tank whereas cleared water is reused through a set of drainage channels to the mineral processing plant. Whether the sludge from the mineral processing plant of the Nanjing YinMao Lead-Zinc Mine contains sulfide minerals is worth testing.

On the basis of the XRD analysis, calcite and quartz were mainly ore minerals in the sludge from the Nanjing YinMao Lead-Zinc Mine. (Figure 3), sulfide minerals were not identified from the XRD spectrum of the sludge. This shows that the sludge from the Nanjing YinMao Lead-Zinc Mine not have the possibility of producing acid mine drainage.

Heavy Metal Contents of the Solid Wastes from the Nanjing YinMao Lead-Zinc Mine

Mine solid wastes may produce acid mine drainage (AMD). AMD contains high concentrations of dissolved metals. The discharge of the AMD may contaminate the soils, ground water and surface water. The mechanisms of acid mine drainage are that pyrite reacts with oxygen and water from the atmosphere, and thereby cause release of acidic, metal-laden leaching

Table 1. Results of the Solid Wastes from the Nanjing Yinmao Lead-zinc Mine by Electron-microprobe (WT%).

Element	Waste Rocks	Tailings	Sludge
O	56.07	57.97	52.19
Mg	1.18	1.43	0.81
Al	1.36	2.50	1.90
Si	15.11	1.85	7.80
S	4.57	5.43	6.86
K	0.34	0.20	0.36
Ca	9.72	20.65	16.25
Mn	6.59	3.63	5.64
Fe	5.05	3.68	7.55
Zn	0.00	0.93	0.00
As	0.00	0.47	0.64
Na	0.00	1.26	0.00

solution. Whether the solid wastes from the mine contain the elements of Fe and S is worth testing.

All solid waste samples from the Nanjing YinMao Lead-Zinc Mine were tested by electron-microprobe. The electron-microprobe test results of all the solid waste samples were presented in Table 1.

According to the Table 1, the waste rocks, tailings and sludge from the Nanjing YinMao Lead-Zinc Mine contain the elements of Fe and S. This shows that the waste rocks, tailings and sludge from the Nanjing YinMao Lead-Zinc Mine have the possibility of producing acid mine drainage.

Extraction Toxicity of the Solid Waste from the Nanjing YinMao Lead-Zinc Mine

Mine solid wastes may produce acid mine drainage (AMD). AMD contains high concentrations of dissolved metals. The discharge of the AMD may contaminate the soils, ground water and surface water. Whether the solid wastes from the mine release toxic elements under acid conditions, the concentrations of toxic elements in the leaching solutions exceed the national standard for hazardous waste identification is worth studying.

The ICP test results of leaching solutions of all the solid waste samples from the Nanjing YinMao Lead-Zinc Mine were presented in Table 2.

According to Table 2, lots of toxic elements such as Cu, Hg, Cr, Cd, Pb, Be, Ba, Ni, Ag and Se were not presented in the leaching solution. The concentrations of Zn and As in the all leaching solution were less than the identification standard for hazardous waste. Thus, all the solid wastes of the Nanjing YinMao Lead-Zinc Mine are not the hazardous waste.

Heavy Metal Contents, Mineralogy and Extraction Toxicity of Solidified Waste from the Nanjing YinMao Lead-Zinc Mine

The Nanjing YinMao Lead-Zinc Mine mixed the tailings and sludges from the mineral processing plant

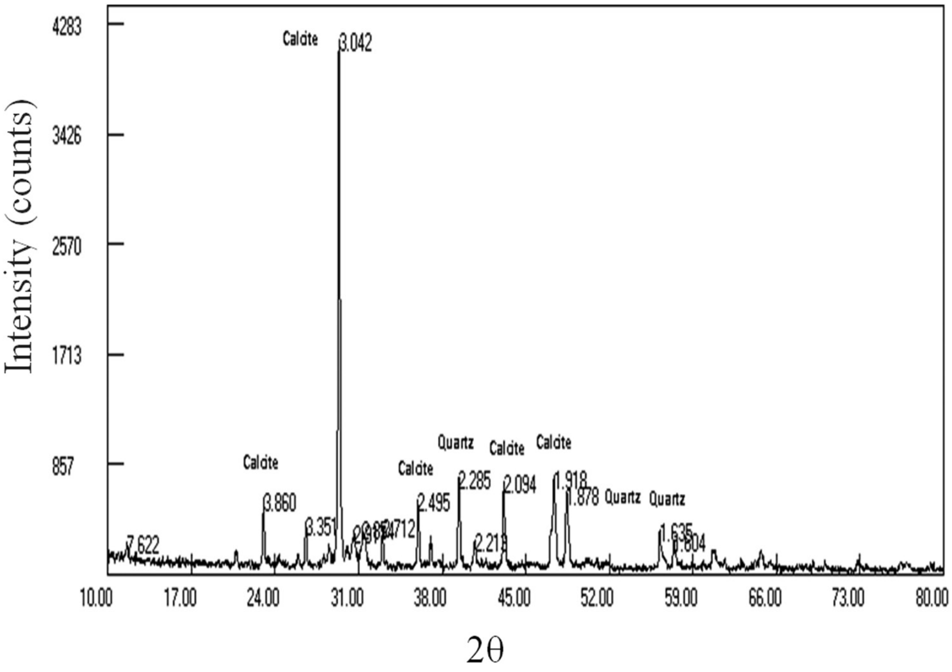

Figure 3. *XRD spectrum of the sludge from the Nanjing YinMao Lead-Zinc Mine.*

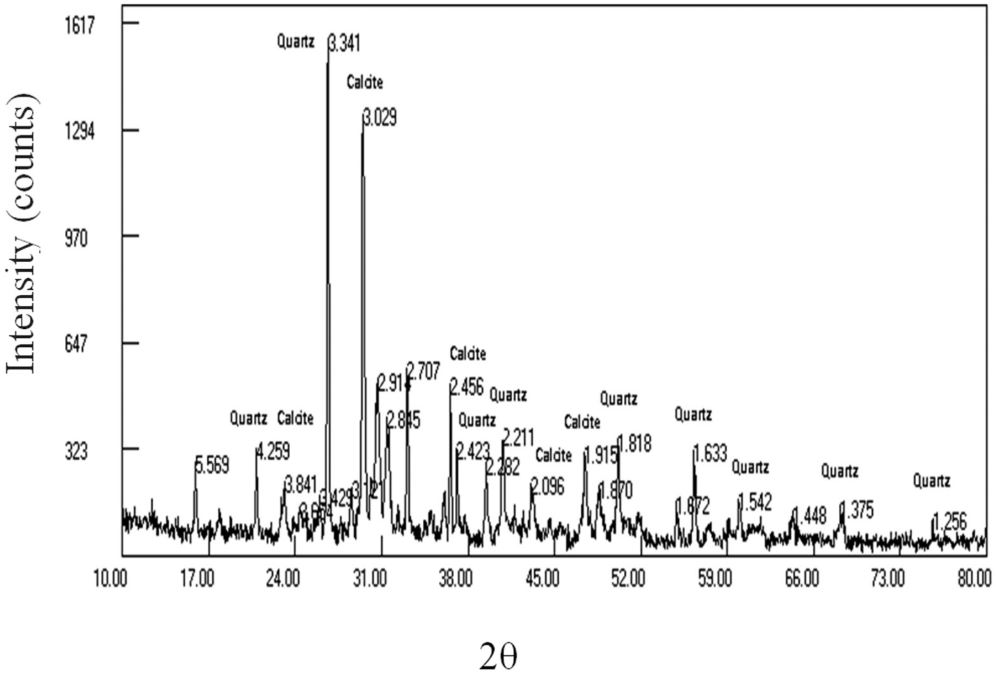

Figure 4. *XRD spectrum of the solidified waste from the Nanjing YinMao Lead-Zinc Mine.*

with ordinary Portland cement (OPC) and backfill the stope by pump. Solidification techniques can reduce the hazard possibility of the solid wastes by converting the contaminants into their least toxic, mobile, or soluble form. Whether the solidified solid waste contains sulfide minerals, contains the elements of Fe and S, releases toxic elements under acid conditions, the concentrations of toxic elements in the leaching solutions exceed the national standard for hazardous waste identification is worth studying.

Table 2. Concentrations of Toxic Elements in the Leaching Solutions of the Solid Wastes by ICP $(MG \cdot L^{-1})$.

Element	Tailings	Waste Rocks	Sludge	Identification Standard for Hazardous Waste*
Cu	0.00	0.00	0.00	100
Zn	0.65	0.00	0.00	100
Cd	0.00	0.00	0.00	1
Pb	0.00	0.00	0.00	5
Cr	0.00	0.00	0.00	15
Hg	0.00	0.00	0.00	0.1
Be	0.00	0.00	0.00	0.02
Ba	0.00	0.00	0.00	100
Ni	0.00	0.00	0.00	5
Ag	0.00	0.00	0.00	5
As	0.00	3.53	3.18	5
Se	0.00	0.00	0.00	1

*According to the China national standard for hazardous waste identification (GB5085.3-2007).

The solidified solid waste sample is tested by electron-microprobe, XRD and ICP.

According to the Table 3, the contents of Al, Si, S, K, Mn, and Fe in the solidified solid waste are less than the contents in the waste rocks, tailings and sludge. Mg, Zn and As are not available. But the content of Ca in the solidified solid waste is high than the content in the waste rocks, tailings and sludge. The solidified solid waste from the Nanjing YinMao Lead-Zinc Mine contains the elements of Fe and S. This shows that the solidified solid waste from the Nanjing YinMao Lead-Zinc Mine has the possibility of producing acid mine drainage.

On the basis of the XRD analysis, calcite and quartz were mainly ore minerals in the solidified solid waste from the Nanjing YinMao Lead-Zinc Mine. (Figure 4), sulfide minerals were not identified from the XRD spectrum of the solidified solid waste. This shows that the solidified solid waste from the Nanjing YinMao Lead-Zinc Mine not have the possibility of producing acid mine drainage.

The results of the ICP test on the stabilized solid

Table 3. Results of the Solidified Solid Waste from Nanjing Yinmao Lead-zinc Mine by Electron-microprobe (%).

O	Al	Si	S	K	Ca	Mn	Fe
61.02	0.51	0.75	0.42	0.17	35.91	0.47	0.75

Table 4. Concentrations of Toxic Elements in the Leaching Solution of Solidified Waste by ICP ($MG\cdot L^{-1}$).

Element	Solidified Waste	Standard for Hazardous Waste Idetification*
Cu	NA	100
Zn	NA	100
Cd	NA	1
Pb	NA	5
Cr	NA	15
Hg	NA	0.1
Be	NA	0.02
Ba	NA	100
Ni	NA	5
Ag	NA	5
As	NA	5
Se	NA	1

NA - data not available.

*According to the China national standard for hazardous waste identification (GB5085.3-2007).

waste indicated that the toxic elements such as Cu, Cd, Pb, Be, Zn, Cr, Hg, Ba, As, Ni, Ag and Se were not available. The concentrations of the toxic elements in the solidified waste were less than the national standard for hazardous waste identification (Table 4). Therefore, the solidified wastes of the Nanjing YinMao Lead-Zinc Mine are not hazardous wastes.

CONCLUSIONS

Detailed characteristics of the solid wastes from the Nanjing YinMao Lead-Zinc Mine situated in the eastern suburb of Nanjing City (China) were investigated in this paper. Results indicated that the solid wastes were not hazardous. Chemical analysis showed that the contents of the toxic elements in the solid wastes were low, which would not cause potential contamination. XRD analyses found that calcite and quartz were mainly ore minerals in the solid wastes, and indicated that the mineralogy of solid wastes was comparatively simple, and the compounds tested by XRD were in good accord with the chemical analysis results. The leaching tests made clear that the solid wastes should not be classified as hazardous wastes because the concentrations of the toxic elements were less than the national standard for hazardous waste identification.

ACKNOWLEDGMENTS

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Residual Levels of Organochlorine Pesticides and Heavy Metals in the Guanzhong Region of the Weihe Basin, North-western China

HONG WEI[1,*], DA HU[1,2], XIAO-LI CHENG[1] and KE-BIN LI[3]
[1]*State Key Laboratory Base of Eco-Hydraulic Engineering in Arid Areas, Xi'an University of Technology, Xi'an, China, 710048*
[2]*China Huadian Electric Power Research Institute, Hangzhou, China, 310030*
[3]*Key Laboratory of Synthetic and Natural Functional Molecular Chemistry of The Ministry of Education, School of Chemistry and Material Science, Northwest University, Xi'an, China, 710069*

ABSTRACT: The residual concentrations of 20 types of organochlorine pesticides (OCPs) is 0.33 to 130.34 ng·g^{-1} (dry mass) in typical soils from 67 orchards spread over six counties in the Guanzhong region of the Weihe Basin, north-western China. Meanwhile, the concentration range of valid state Cu, Zn, and Cd in soil is 0.13 to 1.81 mg·kg^{-1}, ND to 3.96 mg·kg^{-1}, and ND to 0.047 mg·kg^{-1}, respectively. The average residual concentrations of OCPs present a class of multiple order distribution with both latitude and longitude. The residual concentrations of valid state Cu and Zn have some correlation with the residual concentrations of OCPs.

INTRODUCTION

ORGANOCHLORINE PESTICIDES (OCPs) have been recognised as environmental priority control pollutants, as they can become widely distributed in the environment, expand their zone of influence by atmospheric or water-borne means, and produce serious toxicity to creatures [1]. At the same time, OCPs remain a persistent organic pollutant (POP) with among the highest detection rates in the environment. Soil provides strong residence ability and can be a secondary source of OCPs input to the environment. Thus soil plays a vital role in the OCPs global distribution and in the degradation pathway [2]. Soils, meanwhile, suffer from severe pollution by heavy metals: poor mobility and the inability to be degraded by microorganisms mean that such heavy metals (in soil) are long-lasting [3] and pose a serious threat to human health through the food chain. Many studies focused on the pollution state of OCPs and heavy metals in soils. However, the correlation of OCP residue and heavy metals in soils is rarely reported.

Guanzhong Region lies within Shaanxi Province, in north-western China. The Weihe River is the main water source for this region. Organochlorine pesticides were previously used in this region and Weihe River was seriously polluted by organic chemicals [4–6]. Elevated levels of OCPs and heavy metal residues in soils collected from this region have been reported [7–9]. In addition, the Guanzhong region is a fruit-production base, so people are paying more attention to soil pollution and are now testing and evaluating soil environmental quality for green food and pollution-free fruit production. When OCPs and heavy metals accumulate in orchard soils, they affect the growth, fruiting, and lifetime of fruit trees and the quality of their fruit: they pose further hazards to human health through the food chain. So it was deemed necessary to study the correlation of OCPs residues and heavy metals in this region.

This research investigated the distribution, pollution characteristics, and sources of OCPs and heavy metals (Cu, Zn, and Cd) in typical soils from the Guanzhong region in the Weihe basin. A correlative analysis was carried out between OCPs and heavy metals.

MATERIALS AND METHODS

Materials

The test of the residual levels of 20 types of OCPs need the individual standards of corresponding OCPs and the two tracers (TCmX and PCB-209) which were all purchased from Dr. Enrenstorfer (Augsburg, Ger-

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*Author to whom correspondence should be addressed.
E-mail: weihong0921@163.com; Tel: +86 29 82312780

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many). The individual standards of valid state Cu, Zn, and Cd were purchased from Tianjin Aoran Fine Chemical Research Institute. All solvents used were of high-performance liquid chromatography or glass-distilled grade. Florisil, anhydrous sodium sulphate, silica gel and aluminium oxide need to be activated before sample purification. DTPA (diethyltriamine pentaacetic acid, AR), TEA (triethanolamine, AR), anhydrous calcium chloride, and HCl (1 mol/L, 6 mol/L, or 0.1 mol/L) were prepared for the extracting agent to extract the valid state of heavy metals in the soil samples.

Sample Collection

The research area for this study was the Guanzhong region of Weihe Basin. Typical soil samples were collected, from 67 orchards spread over six counties within the research area, in February 2013. The location of sampling points and their planting types are summarised in Table 1. and Figure 1. The soil samples were collected the top 20-cm by a stainless steel grab-sampler, preserved into polytetrafluoroethylene bags and kept at –20°C before tested.

Table 1. Soil Samples: Locations and Sample Descriptions.

County	Sample Code	Land Planting Type
Xingping	X1–X3, X12	peach
	X4–X5	apricot
	X6–X11	apple
Fufeng	F1–F15	apple
	F16–F18	kiwi
Weinan	W1–W3	grape
Zhouzhi	Z1, Z3–Z6, Z8–Z9, Z11, Z13–Z15	kiwi
	Z2, Z7, Z10, Z12	peach
Huxian	H1, H5–H7	grape
	H2–H4	melon
	H3	cherry
	H8–H11	peach
Lintong	L1–L5	pomegranate
	L6	mulberry
	L7	pear
	L8	peach

67 orchards and 10 land planting types.

Determination of OCP Residues by GC-ECD

A 20.0 g freeze-dried soil sample was extracted by Soxhlet apparatus with surrogate standards (TC_mX), PCB-209, and 120 mL methylene chloride for 24 h. The extract need to be concentrated, further solvent-exchanged to hexane, purified with home-made purification column, nitrogen flowed and analyzed by GC-ECD. The injector temperature was 250°C, detector temperature was 300°C and carrier gas was He at |1.0 mL·min^{-1}. The temperature-rising program were as follows:

$$\text{Initial temperature: } 90^{\circ}\text{C, held for 5 min}$$

$$90^{\circ}\text{C} \xrightarrow{10^{\circ}\text{C/min}} 160^{\circ}\text{C}$$

$$160^{\circ}\text{C} \xrightarrow{2^{\circ}\text{C/min}} 220^{\circ}\text{C, held for 8 min}$$

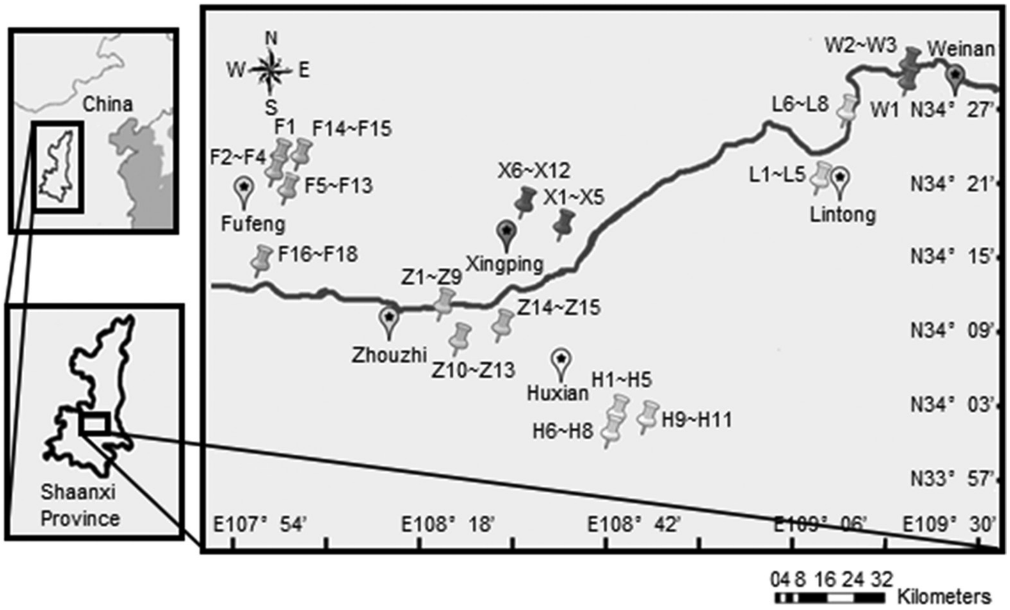

Figure 1. Map of soil sample locations represented within the Guanzhong region of the Weihe River.

Table 2. OCPs Residues in Typical Soils from the Guanzhong Region, Weihe Basin, China (ng·g^{-1}).

Target Chemical	Min.	Max.	Mean
α-HCH	ND	0.91	0.11
β-HCH	ND	8.00	0.58
γ-HCH	ND	77.33	1.34
δ-HCH	ND	4.86	0.19
ΣHCHs	0.01	86.16	2.22
op′-DDE	ND	1.34	0.15
p,p′-DDE	0.055	29.61	3.72
o,p′-DDD	ND	8.12	0.29
p,p′-DDD	ND	14.78	1.43
o,p′-DDT	0.0025	1.48	0.20
p,p′-DDT	ND	49.42	1.86
ΣDDTs	ND	80.90	7.65
TC	ND	2.62	0.19
CC	ND	1.60	0.09
ΣCHLs	ND	4.22	0.29
α-endosulfan	ND	0.29	0.02
β-endosulfan	ND	0.52	0.04
Σendosulfan	ND	0.78	0.07
heptachlor	ND	1.55	0.07
heptachlor epoxide	ND	0.78	0.03
aldrin	ND	4.15	0.13
dieldrin	ND	1.99	0.14
endrin and endosulfan sulfate	ND	4.42	0.45
ΣOCPs	0.33	130.34	11.05

ND: not detected, or lower than possible detection limit(s).

Determination of Valid State Cu, Zn, and Cd

The extracting agent was composed of: 1.967 g DTPA, 14.92 g TEA, 1.11 g anhydrous calcium chloride, and approximately 950 mL deionised water. Then the pH was adjusted to 7.3 using HCl and a 1.0 g soil sample was stirred at 180 ± 20 rpm with 5.0 mL of the extracting agent at 25 ± 2°C for 2 h to extract the valid state Cu, Zn, and Cd from these soils. After the extracting agent was filtered to remove soil particles, it was subjected to quantitative analysis by atomic absorption spectrophotometer equipped with an acetylene-air burner and a hollow cathode lamp.

RESULTS AND DISCUSSION

Residual Level of OCPs

The detection results for twenty target OCPs in the soil samples showed that the detection rate of HCHs, DDTs, CHLs, and other OCPs in all samples were 100%, 97%, and 33 to 84%, suggesting that the orchards soils were generally polluted by HCHs, DDTs, and CHLs. The residual levels of 20 types OCPs are listed in Table 2: the concentrations of OCPs were 0.33 to 130.34 ng·g^{-1} (dry mass) with a mean of 11.05 ng·g^{-1}. The concentration of HCHs (sum of four types of HCHs was 0.0097 to 86.16 ng·g^{-1}, average value 2.22 ng·g^{-1}) was lower than that of DDTs (sum of six types of DDTs, 0.16 to 80.90 ng·g^{-1}, average value 7.65 ng·g^{-1}). Major types of residual HCHs were *γ*-HCH and for DDTs were *p,p′*-DDT, *p,p′*-DDD, and *p,p′*-DDE. The concentrations of HCHs could meet the requirements of Level I of the soil environmental quality standard (GB15618-1995) except at F2. DDT concentrations could reach Level I, expect at F4. On the whole, the status of OCPs in orchards soils was similar to that in the Hexi corridor, Gansu Province and Lanzhou Region, and was lower than that in other regions reported in China (Table 3).

Spatial Distribution of OCPs

The residual levels of OCPs varied across all samples: the average levels in all samples decreased as follows: Fufeng (20.50 ng·g^{-1}), Huxian (13.06 ng·g^{-1}), Zhouzhi (7.79 ng·g^{-1}), Lintong (5.17 ng·g^{-1}), Weinan (4.86 ng·g^{-1}), and Xingping (4.56 ng·g^{-1}). Xingping, Weinan, and Lintong had similar polluting level of OCPs. The concentration level sum ΣOCPs in 29.85% of soil samples was higher than the average concentration and 45.0% of these soil samples were collected from Fufeng. For example, the OCP residue concentration at F2 was 130.34 ng·g^{-1}, which was the highest of all samples; secondly, the residual concentration of OCPs at F4 was 82.24 ng·g^{-1}, including 1.24 ng·g^{-1} as ΣHCHs, 80.90 ng·g^{-1} as ΣDDTs, and 0.057 ng·g^{-1} as ΣCHLs. Thus the pollution status of OCPs in Fufeng was more serious than in other regions. Nevertheless, the average concentration of residual HCHs in Fufeng was comparable with residual levels in Guangdong Province and Xingjiang Region and was far lower than that in Fuzhou. The average concentration of residual DDTs in Fufeng was higher than that in Guangdong Province, Nanjing, and Gansu Province, but was much lower than that in Xinjiang and Fuzhou (Table 3).

In Figure 2, the X-axis represented latitude, the Y-axis represented longitude, and the Z-axis represented the mean OCPs residual concentration. The spatial distribution trend of OCPs average residual concentrations from six areas in this study was projected on the YZ-plane and presented as "*W*", which suggested that fluctuations in residual OCPs concentrations in the east-west direction were violent. The spatial distribu-

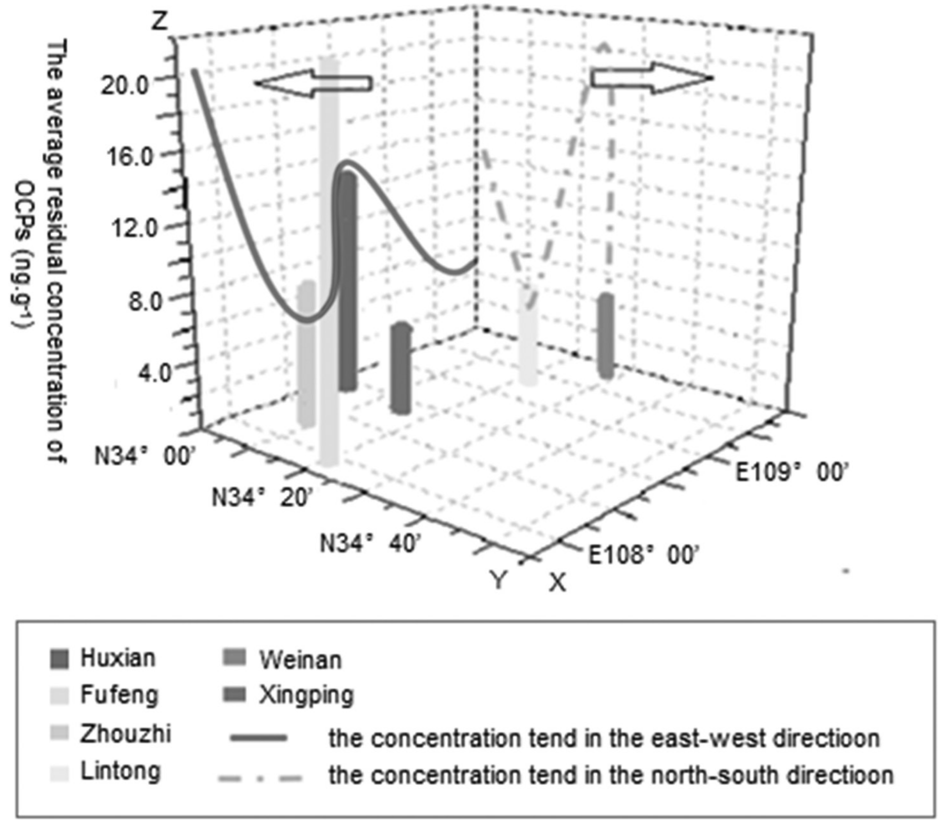

Figure 2. *Trend analysis of OCP residues in soils from the Guanzhong region, Weihe Basin.*

tion trend projected on the XZ-plane suggested that the fluctuations in the north-south direction were greater than those in the east-west direction. In brief, the results indicated that the trend of OCP average residual concentration in the Guanzhong Region of Weihe Basin was a multiple-order distribution in both latitude and longitude.

Residual Level of Valid State Cu, Zn, and Cd

The range of concentrations of valid state Cu, Zn, and Cd in typical soils was from 0.13 to 1.81 mg·kg^{-1} (average value 0.45 mg·kg^{-1}), ND to 3.96 mg·kg^{-1} (average value 0.75 mg·kg^{-1}), and ND to 0.047 mg·kg^{-1} (average value 0.013 mg·kg^{-1}), respectively.

Table 3. Comparison of OCPs Concentrations in Typical Soils from the Guanzhong Region, Weihe Basin, and Other Regions of China (ng·g^{-1}).

Location	ΣHCHs	ΣDDTs	Year	Reference
Agricultural soils (typical areas) Guangdong Province	ND~104.35 (5.90)	ND to157.75 (10.18)	2002~2005	[11] (2007)
Soils in Baguazhou: non-polluted food base in Nanjing	2.48 to 17.80 (6.02)	3.36 to 74.19 (12.61)	2005	[12] (2007)
Soils of typical agricultural regions in Xinjiang	0.37 to 22.82 (5.94)	0.91 to 858.47 (95.11)	2010	[13] (2012)
Hexi corridor, Gansu Province and Lanzhou region	0.07 to 9.16 (1.32)	0.22 to 53.69 (8.58)	2011	[13] (2012)
Vegetable soils, Fuzhou	ND to 115 (21.1)	4.63 to 298 (55.7)		[14] (2012)
Typical soil, Guanzhong region, Weihe Basin	0.0097 to 86.16 (2.22)	0.16 to 80.90 (7.65	2013	This study
Xingping	0.0097 to 2.43 (0.65)	0.16 to 11.63 (2.44)		
Zhouzhi	0.026 to 2.56 (0.50)	1.03 to 29.22 (6.84)		
Fufeng	0.11 to 86.16 (5.44)	1.63 to 80.90 (14.45)		
Weinan	0.23 to 0.45 (0.31)	2.20 to 4.31 (3.23)		
Lintong	0.27 to 0.85 (0.62)	0.88 to 6.58 (2.67)		
Huxian	0.11 to 14.21 (2.70)	0.84 to 28.33 (8.11)		

ND: not detected, or lower than possible detection limit(s).
Data representation: minimum to maximum (mean).

Table 4. Comparison of Valid State Cu, Zn, and Cd Concentrations in Typical Soild from Guanzhong Region, Weihe Basin, and Other Regiond of China (ng·g^{-1}).

Location	Cd	Cu	Zn	Reference
Garden plot, Kunshan City, Jiangsu Province	0.103a	4.93a	–	[15] (2010)
Vegetable soil, Jiangbei area, Nanjing City	0.06a	5.62a	5.36a	[3] (2010)
Vegetable soil from wastewater irrigated area, Beijing-Tianjin city cluster	0.46a	24.5a	97.3a	[16] (2012)
Urban soils, Yibin City	–	56.35a	133.88a	[17] (2012)
Background soils, Shanxi Province	0.76	21.4	69.4	[18] (1990)
Level II standard:environment quality standard for soils (GB15618-1995)	0.60	200 (orchard, pH > 7.5)	300	[10] (1995)
Typical soil, Guanzhong Region, Weihe Basin	0.047a	0.45a	0.75a	This study (2013)
FuFeng	0.012a	0.309a	0.536a	
Huxian	0.009a	0.389a	0.914a	
Lintong	0.008a	0.473a	0.501a	
Xingping	0.015a	0.583a	1.259a	
Weinan	0.014a	0.356a	0.302a	
Zhouzhi	0.013a	0.339a	0.478a	

a: mean value.

The average residual levels in all samples decreased in the following order: Zn, Cu, and Cd. The concentrations of valid state Cu, Zn, and Cd were much lower than the secondary standard values in the relevant soil environmental quality standard (GB15618-1995). The concentrations of Cu, Zn, and Cd were lower than in other regions of China. It was speculated that the studied areas may be not polluted by heavy metals at this early stage and that their migration was the main anthropogenic input. The residual levels of valid Cu, Zn, and Cd from Xingping stood out among the other areas (Table 4).

The residual concentrations of valid state Cu, Zn, and Cd in each soil sample were analysed by Kolmogorov-Smirnov test using SPSS 19.0 to identify the distribution state of these residual levels. The residual concentrations of valid state Cd ($p = 0.321$) conformed to the normal distribution, but the distributions of Cu and Zn did not. There was a positive (Pearson) correlation between the residual concentrations of Cu and Zn: the correlation coefficient was 0.549 ($p = 0.000$) which indicated that the valid state Cu and Zn were likely to have the same source.

Correlation between OCPs and Heavy Metals

The correlation between OCPs and heavy metals found with SPSS 19.0 was studied to ascertain whether or not there were synergistic or antagonistic effects between them in these soils. The residual concentration of OCPs and Cu, Zn, and Cd in each soil sample did not conform to the normal distribution except in the case of Cu. The correlation between OCPs and heavy metals was analysed by Spearman correlation (rank correlation) analysis.

The correlation coefficients of the residual concentrations of valid state Cu with heptachlor and *p,p′*-DDT were 0.293 ($p = 0.048$) and 0.298 ($p = 0.044$), separately. The values of these two correlation coefficients were lower than 0.3, indicating that the valid state Cu exerted some influence on the heptachlor, and *p,p′*-DDT, residues, but that the extent thereof was negligible. The residual concentrations of Cu were also related to *p,p′*-DDE (correlation coefficient 0.369, $p = 0.012$), *α*-endosulfan (correlation coefficient –0.499, $p = 0.000$), *β*-endosulfan (correlation coefficient –0.372, $p = 0.011$), and dieldrin (correlation coefficient –0.303, $p = 0.041$), respectively. The rank correlations between valid state Cu and *p,p′*-DDE, α-endosulfan, *β*-endosulfan, and dieldrin separately were low according to the absolute value of these correlation coefficients which ranged from 0.3 to 0.5. It suggested that the valid state Cu in soil exerted a low, positive, influence on the residues of *p,p′*-DDE and dieldrin, yet had little influence on the residues of α-endosulfan and *β*-endosulfan. Meanwhile, the residual concentrations of valid state Zn had low and inverse correlations (rank correlation) with the residual concentrations of *α*-endosulfan (correlation coefficient –0.456, $p = 0.002$). Overall, the influence of the valid state Cu on OCP residues was greater than that of Zn and Cd.

CONCLUSIONS

The residual levels, and distribution status, of OCPs and heavy metals in typical soils from the Guangzhong region of the Weihe Basin were investigated. It was found that the average OCPs concentrations from Fufeng were the highest and the residual levels of valid Cu, Zn, and Cd in soils from Xingping stood out among the other areas. The valid state Cu, Zn, and Cd may be not polluted at this early stage and migration may be the main input coupled with strong anthropogenic influence. The correlation between valid state Cu and OCPs residues was better than that for valid state Zn and Cd.

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Imidazoline Corrosion Inhibitor in Metal Acid-Phase Reactors in Anaerobic Digestion

GONGZHAO LIU*, ZHENSHENG YANG, LINNAN ZHANG and KEQIANG QIU
Shenyang University of Technology, School of Science, Liaoning 110870, China

ABSTRACT: Acid-phase reactors in anaerobic digestion are widely used for treating solid waste such as kitchen waste and sludge. The purpose of this study was to find the optimum control parameters for corrosion behavior in-vessel .Various physical and chemical parameters were monitored to evaluate water soluble imidazoline inhibitor effect on the microbial communities in acid fermentation of sludge and corrosion inhibitors for steel alloy. The metal products pieces were tested by surface-active agents with corrosion inhibitors in low molecular weight organic acids, mixing with NH_4Cl-NH_4HS-H_2O to simulate the sludge and acid waste. Results show that water soluble imidazoline materials are a kind of excellent performance corrosion inhibitor, which can meet the requirements of environmental protection and has no adverse effect on metal containers and fermentation process. Inhibition of corrosion by adding an imidazoline ranging in 10–20 mg/L at temperature below 100°C is limited. The influence of temperature on inhibition is small.

INTRODUCTION

SEALED VESSEL ANAEROBIC DIGESTION is a controlled environmental composting and for sludge and other organic waste. Their biggest characteristic and the most attractive property of this method is the small impact on the surrounding environment [1,2]. Reactor designs for sealed vessel anaerobic digestion has evolved over time. The basic design has historically been is a cylinder-shaped main reactor with a domed top. There is usually a dome at the top of the main cylindrical reactor and solid waste is fed into the reactor through a port connected to the bottom of the reactor. Because the kitchen waste and sludge contains large amounts of bacteria, thus sealing type compost using anaerobic way. Bacterial is often killed by high temperature generated by the pile body [3]. In anaerobic digestion, acid genesis which involves the bacterial conversion of the hydrolysis products into lower molecular intermediate compounds. The acid genesis responsible for this transformation is mainly obligate anaerobes.

The intermediate compounds produced low molecular weight organic acids such as acetic, propionic, butyric, valeric and caproic acids, as well as small amounts of formic acid and lactic acid. Some aldehydes, ketones, ammonia, carbon dioxide, hydrogen, and water are also produced by acid-forming bacteria [4–6] a. In those process vessels metal corrosion is an issue for the acid and hazardous circumstance [7,8]. Therefore, many research works has been focus on the formation of inhibition film on the metal surface to protect it from corrosion [9]. The inhibition efficiency of organic compounds has relevance with their adsorption properties to the metal surface, which includes many factors, such as metal surface property, active group chemical structure of inhibitor [10]. Many imidazoline derivatives have been used as metal corrosion inhibitors and especially primarily applied in the petrochemical plants and wells and corrosion mechanism of it was also widely research and analysis recently to know how it works [11,12].

Imidazoline inhibitor as a new green corrosion inhibitor has wide application due to its with low toxicity and, lightness pollution, became widely used [13]. Oil soluble imidazoline inhibitors technology is relatively mature at home and abroad, but the cost is high. Additionally, and with oil as a solvent, it may pose generate a certain risk in the process of storage and transportation, with oil as a solvent [14].

Water soluble imidazoline is a type of green inhibitor developed in recent years. It is developed from oil soluble imidazoline by introducing water soluble group [15]. It has many advantages: the imidazoline ring is a

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*Author to whom correspondence should be addressed.
E-mail: 707460916@qq.com

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plurality of the nitrogen atom of the lone pair electrons and metal iron empty orbital coordination bond formation, one layer of protective film can be produced and another layer of oil film is produced. The two-layer protective film aims to prevent the corrosive medium in contact with the metal surface. It has many other favor properties, e.g., low toxicity, little pollution; using water as the solvent, low cost and no storage concern; a neutralizing agent mixed together [16].

In this paper, corrosion inhibitor behavior of water soluble imidazoline in corrosion medium (corrosion dynamics scour static weight-loss method, scanning electron microscopy, polarization curves, XRD) was investigated.

MATERIALS AND EXPERIMENTAL

Materials and Corrosion Medium

Chemicals used in this research work were analytical reagent and get from China Pharmaceutical. Water-soluble amide imidazoline was synthesized by nonanoic acid, glacial acetic acid, using n-butyl alcohol as the solvent.

Corrosion medium is low molecular weight organic acids (C_{HCOOH} = 150 mg/L, $C_{CH3COOH}$ = 150 mg/L) mixing with NH_4Cl-NH_4HS-H_2O. The sludge and acid waste was stimulated with a pH value 2.5. Test rods contained 0.045% P, 0.38% Si, 1.4% Mn, 0.22% C beside Fe cutting from sheets of low carbon steel. The electro-polarization and weight loss were test by remain steel rods.

Experimental Design for Weight Loss

Weighing metal specimen was conducted in experimental medium, under specified conditions of soaking for a certain period of time. The test piece was then removed, cleaned and dried after weighing. The average corrosion rate was calculated based on mass loss test piece. Installation diagram for Static weight-loss method was shown in Figure 1.

The corrosion rate was calculated using Equation (1):

$$R = \frac{8.76 \times 10^7 \times (M_0 - M)}{S \times T \times D} \quad (1)$$

S = Surface area
T = is Time
D = Density of test piece material

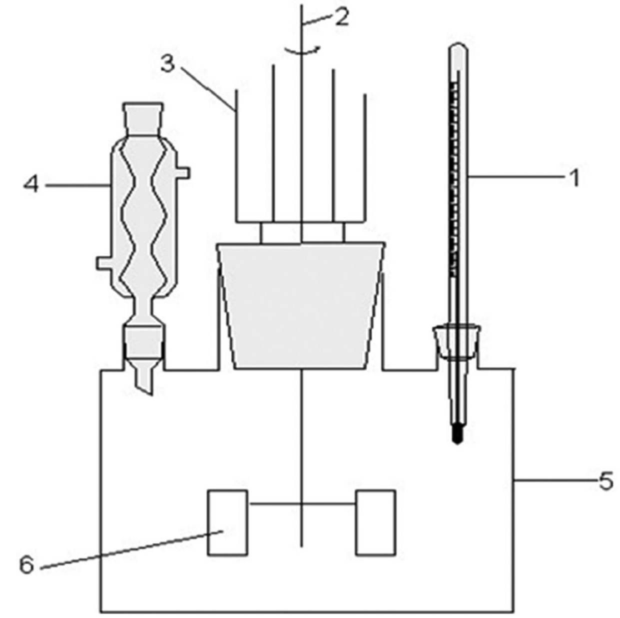


Figure 1. *Static weight-loss method installation diagram: 1 - thermometer, 2 - stirring shafts, 3 - liquid seal , 4 - condenser, 5 - mspecial bottle with three mouths and 6 - hanging piece.*

The corrosion ratio was calculated using Equation (2):

$$\eta_1 = \frac{\Delta m_0 - \Delta m_1}{\Delta m_0} \times 100 \quad (2)$$

Static Potential Polarization

In strong polarization regions, the horizontal coordinate corresponding to the intersection of anode. Cathode polarization curves obtained through Tafel extrapolation linear region is the logarithm of the corrosion current density. To obtain the corrosion current density, Faraday's law was used. To obtain the corrosion rate, by not adding and with corrosion rate calculation of the corrosion current density and corrosion inhibitor; at the same time corrosion potential and polarization curve were used to determine the role type corrosion inhibitor.

The corrosion rate calculation was based on Equation (3):

$$R = \frac{8.76 \times 10^4 \times i_c \times M}{n \times F \times p} \quad (3)$$

N = Electronic number
F = Faraday’s constant
P = Potential

The corrosion rate was calculated based on Equation (4):

$$\eta_2 = \frac{i_{c0} - i_{c1}}{i_{c0}} \times 100 \qquad (4)$$

The electro-polarization technique was applied with the use of a Radiometer analytic Potential. The concentration of imidazoline derivatives employed ranged from 0 to 20 ppm in low molecular weight organic acids, mixing with NH_4Cl-NH_4HS-H_2O.

The chemical structure of the synthesized compounds was determined by the following steps.

1. Scanning electronic microscope was used to observe morphology of carbon steel specimen surface, using SU8010 in Analytic Center at Shenyang University of Technology.
2. Potential static method was used for electrolytic cell for three electrode systems, the working electrode for the seal on the electrode frame of carbon steel. The area is 1 cm^2. The Pt and saturated potassium chloride were used as the auxiliary electrode and reference electrode respectively, voltage range of which is –1 to 0V. The scanning speed is 0.01V/s, CHI604 electro-chemical measurement Analytic Center, Shenyang University of Technology.

RESULT AND DISCUSSION

Result of Weight Loss Experiment

Effect of addition of imidazoline inhibitor on corrosion rate was examined at room temperature for 72 h in the low molecular weight organic acids, mixing with NH_4Cl-NH_4HS-H_2O to simulate the composting medium corrosion medium as shown in Figure 2. With increasing concentration of those chemicals, corrosion rate decreased and inhibitor rate increased.

In the corrosion medium, inhibition effect for carbon steel corrosion due to addition of minor imidazoline amide increased with increasing imidazoline dose. The corrosion rate decreased gradually, while imidazoline concentration reached 10 ppm. The inhibition rate reached more than 80% at the same time by measuring the blank specimen found in corrosive medium surface with continuous bubbles. This may due to the reaction of the acid and iron corrosion medium test piece, producing hydrogen and adding corrosion inhibitor specimens in the solution. This might not be observed after cleaning the surface of test piece. A certain amount of corrosion spots and stripes were observed while the concentration was greater than 10 ppm. Therefore the most appropriate concentration should fall within the range of 10–20 ppm.

Table 1 shows that, with the same dose, the synthe-

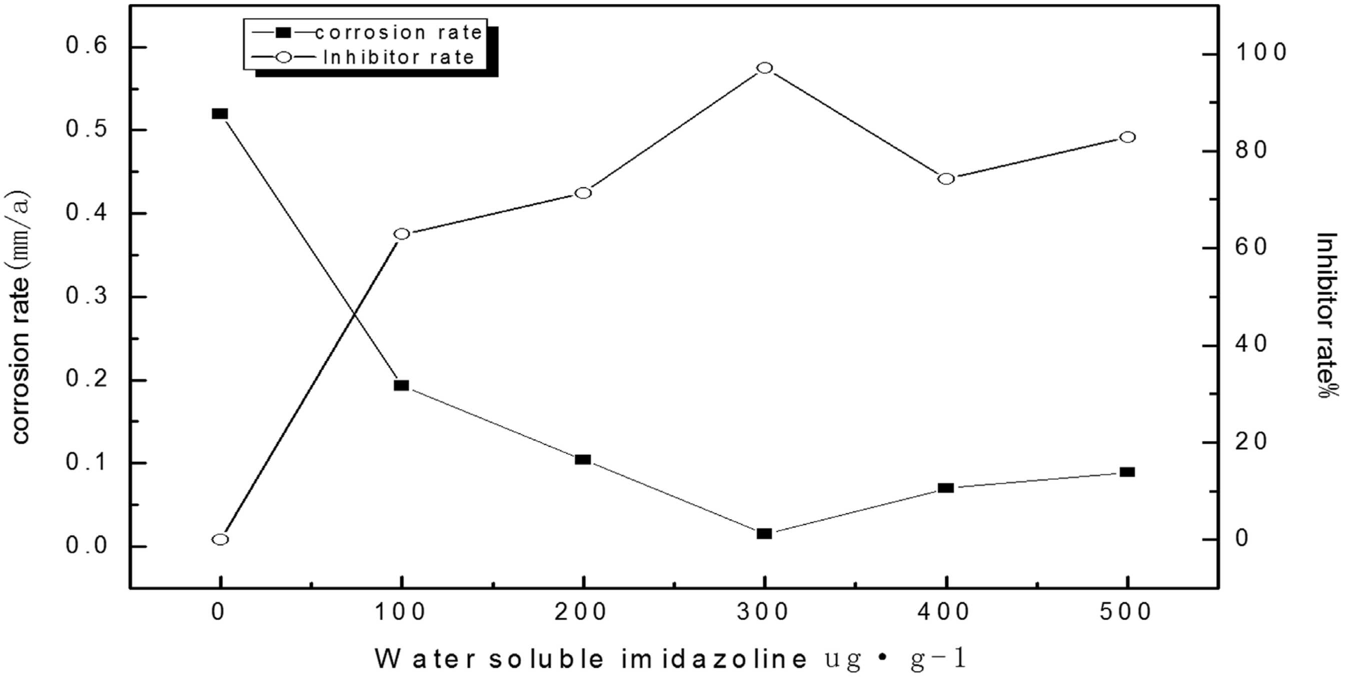


Figure 2. Effect of dose on corrosion rate.

Table 1. Comparison of Different Types of Inhibitor.

Target Chemical	**Blank Weight Loss**	**Additive Weight Loss (g%)**	**Inhibition Rate (%)**
Blank	0.0386		
Fatty acid		0.0204	47.15
Oil soluble imidazoline amide		0.0151	60.88
80%WS female agent + 20%T154		0.0140	63.73
50%WS female agent + 50%T154		0.0132	65.80
Water soluble imidazoline amide		0.0148	61.66

sis of water soluble imidazoline amide corrosion inhibitor on corrosion inhibition rate reached 61.66%. The corrosion rate is not very different for oil soluble imidazoline, inhibition rate 14% of which is higher than that of fatty amide.

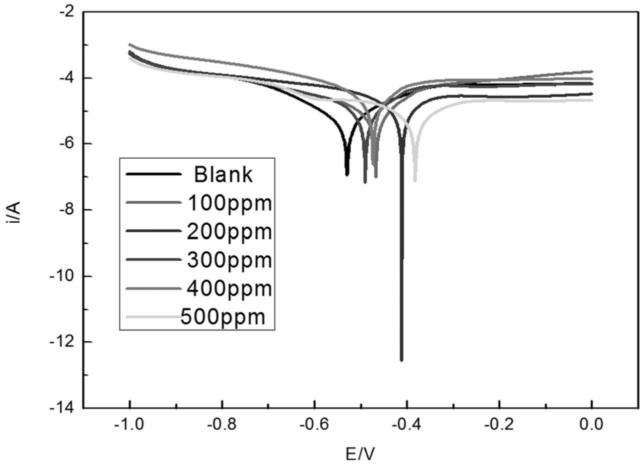
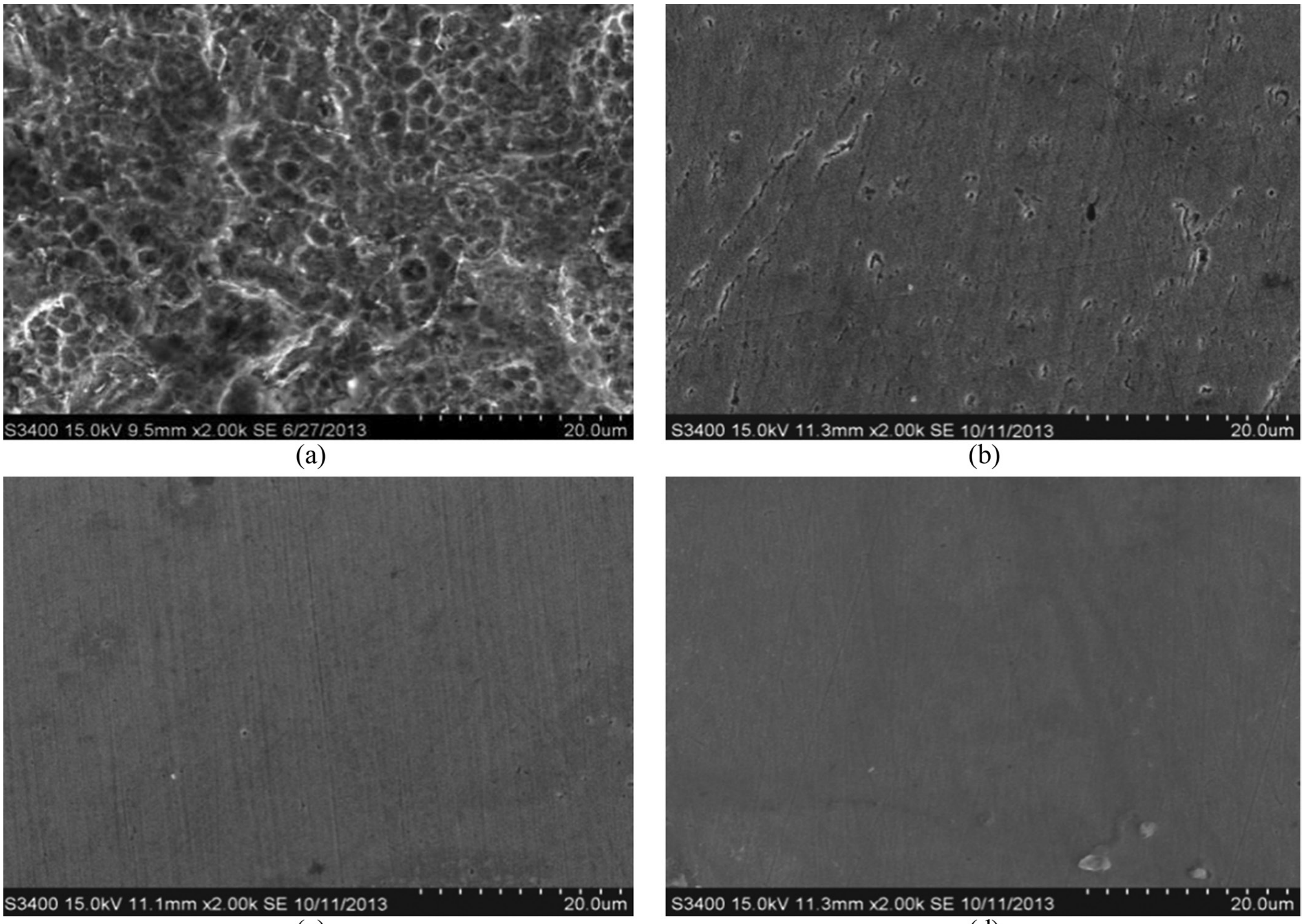


Figure 3. *Effect of imidazoline dose on the inhibition rate.*

Result of Static Potential Polarization Method

Figure 3 shows the impact of imidazoline dose, the mixed solution conditions, and the anodize process are controlled by the active dissolution of Fe. This is not due to varying concentration of cathodic process for polarization to H^+. The same polarization potential was observed. The imidazoline dose increased



(a) (b)

(c) (d)

Figure 4. *SEM of different corrosion inhibitor dose: (a) 0 mg/L; (b) 5 mg/L; (c) 10 mg/L and (d) 20 mg/L.*

when the cathodic current density decreased, and the cathodic depolarization process decreased. The corrosion potential decreased when imidazoline dose and solution acidity cathodic depolarization process decreased, leading to the corrosion potential shifts actively. In addition, the corrosion current density decreased significantly with increasing imidazoline dose. With higher concentration of acid acetic, the cathodic depolarization process intensifies, resulting to a higher corrosion rate.

Corrosion Inhibition Performance Evaluation Results

Figure 4 shows that, with the increase of corrosion inhibitor dose, corrosion inhibition rate had been improved to a certain extent.

The inhibitor concentration was 5 mg/L and the specimen surface is 10 mg/L on pitting spots. While the addition of inhibitor concentration is 15 mg/L and 20 mg/L the specimen surface is flat.

CONCLUSIONS

1. The water solvable imidazoline inhibitor synthesized by surface active agent compounds showing favorable inhibiting properties of corrosion protection for low carbon steel in 0.1M low molecular weight organic acids mixing with NH_4Cl-NH_4HS-H_2O, which simulated the sludge and acid waste solutions at room temperature. With increasing of inhibitors concentration, the inhibition efficiency was also growth up.
2. The weight loss method was utilized to evaluate corrosion medium age. When concentration of adding mass was 10 mg/L, the inhibition rate was more than 80%.
3. The inhibition effect of thalidomide imidazoline corrosion increased by adding a suitable for 1–20 mg/L at a temperature below 100°C. The inhibition effect of temperature is limited.

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Table 5. Comparison of state-of-the-art matrix resins with VPSP/BMI copolymers.

Resin System	Core Temp. (DSC peak)	T_E	Char Yield, %
Epoxy (MY720)	235	250	30
Bismaleimide (H795)	282	>400	48
VPSP/Bismaleimide copolymer			
C379: H795 = 1.9	245	>400	50
C379: H795 = 1.4	285	>400	53

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