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# Feasibility of disposing waste glyphosate neutralization liquor with cement rotary kiln

Y. Bai[a,b], Y.B. Bao[a,b], X.L. Cai[a,b], C.H. Chen[a,b], X.C. Ye[a,b,*]

[a] College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China
[b] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, China

## HIGHLIGHTS

- The waste neutralization liquor was injected directly into the kiln system.
- No obvious effect on the quality of cement clinker.
- The disposing method was a zero-discharge process.
- The waste liquor can be used as an alternative fuel to reduce the coal consumption.

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## ABSTRACT

The waste neutralization liquor generated during the glyphosate production using glycine-dimethylphosphit process is a severe pollution problem due to its high salinity and organic components. The cement rotary kiln was proposed as a zero discharge strategy of disposal. In this work, the waste liquor was calcinated and the mineralogical phases of residue were characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD). The mineralogical phases and the strength of cement clinker were characterized to evaluate the influence to the products. The burnability of cement raw meal added with waste liquor and the calorific value of waste liquor were tested to evaluate the influence to the thermal state of the kiln system. The results showed that after the addition of this liquor, the differences of the main phases and the strength of cement clinker were negligible, the burnability of raw meal was improved; and the calorific value of this liquor was 6140 J/g, which made it could be considered as an alternative fuel during the actual production.



## 1. Introduction

Glyphosate is a widely used herbicide because of its low toxicity and high efficiency [1], which could be synthesized in many different ways [2–6]. As the biggest producer and exporter in the world, China occupies more than 70% of the world's gross output, and the capability is about 720 thousand tons [7]. The most widely employed synthetic method in China is glycine-dimethylphosphit process. More than 70% of the total output is produced in this way [8]. But waste neutralization liquor (abbreviated as WNL), containing glyphosate, organic mixtures, NaCl and other salts, would be produced inevitably at the same time, which could cause soil salinization and water eutrophication. And to produce 1 ton of glyphosate, about 5 tons WNL would be generated. It would be a serious pollution problem if discharged directly to the environment.

Various methods were developed to deal with these kinds of hazardous materials. The landfill was used to be a common and economical way to deal with large amount of waste, but many landfills would be closed in the near future, and the existing ones need to be covered [9,10]. There are also some specific ways to deal with the WNL, such as nanofiltration [8], advanced oxidation degradation [11–14], adsorption technology [15], etc. And some researchers tried to employ bipolar membrane electrodialysis (BMED) for glyphosate recovery from WNL [16]. Nonetheless, none of the mentioned methods could totally eliminate the WNL, while the disposing capacity was limited and the cost was relatively high.

Rotary kiln is an energy intensive facility obtaining a high temperature by the combustion of fossil fuel. It has been used as waste incinerator with the aim of destructing hazardous and other

* Corresponding author at: College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China. Tel.: +86 25 83172122.
*E-mail address:* yexuchu@njtech.edu.cn (X.C. Ye).

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**Table 1**
Main composition of the waste neutralization liquor.

| Item | Value | Item | Value |
|---|---|---|---|
| pH | 12.17 | Glyphosate (g/L) | 13.02 |
| TOC (g/L) | 23.36 | NaCl (g/L) | 163.66 |
| COD (g/L) | 63.64 | $PO_3^{3-}$ (g/L) | 18.24 |

**Table 2**
Chemical compositions of the cement raw meal.

| Chemical composition | CaO | $SO_2$ | $A1_2O_3$ | $Fe_2O_3$ | MgO | KH | SM | IM |
|---|---|---|---|---|---|---|---|---|
| wt.% | 44.19 | 13.76 | 3.16 | 2.13 | 0.86 | 0.993 | 2.6 | 1.49 |

difficult waste streams [17]. Meanwhile, the rotary kiln is an essential facility of the dry process cement production, which is integrated in the cement kiln system. Thanks to its high incinerating temperature, long incinerating time and large capacity, it has been employed to dispose various types of waste [18–23] as a zero discharge method.

However, the cement clinker would certainly be affected by the adding of waste with complex components, such as the fly ash from municipal solid waste (MSW). The produced clinker needs to be tested to ensure the quality [24,25].

Similarly, the WNL has complex components, which might cause influences on the qualities of cement clinker. And the thermal state in the kiln system would also be affected due to the calorific value of WNL. In this paper, firstly the residue of WNL after calcination was observed by SEM and the main components were determined by XRD. Furthermore, the mineralogical phases and strength of cement clinker were characterized, and the burnability of the cement raw meal and the calorific value of WNL were tested, in order to evaluate the feasibility of disposing WNL with cement rotary kiln system.

## 2. Experimental

### 2.1. Materials

The WNL was provided by a glyphosate manufacturer in Zhejiang China, whose synthetic route was glycine-dimethylphosphit process. The producing condition was steady which could ensure the component of WNL was consistent. And the main composition was characterized by following the methods in [8,16]. The results were shown in Table 1. The glyphosate would decompose at 187 °C [26], so the calcination temperature was set at 150 °C, 250 °C, 350 °C, 450 °C and 550 °C, respectively, among which the 150 °C calcination could avoid the decomposition of glyphosate. Residue at 550 °C was observed by scanning electron microscope (SEM), and then ground into 80 μm powders, in order to make sure it could be mixed with cement raw meal uniformly. And the mineralogical phases were furthermore determined by X-ray diffraction (XRD).

The powder of cement raw meal provided by a cement plant was 80 μm, which was dried at 105 °C for 24 h. The chemical compositions were reported in Table 2, and the cement moduli, including lime saturation factor (KH), silica modulus (SM) and iron modulus (IM), were listed too. In which, $KH = (CaO-1.65Al_2O_3-0.35Fe_2O_3)/(2.8SiO_2)$, $SM = SiO_2/(Fe_2O_3 + Al_2O_3)$, and $IM = Al_2O_3/Fe_2O_3$.

### 2.2. Sample preparation

Four different groups of samples containing WNL residue powder were prepared, as shown in Table 3. The residue used here was obtained at 550 °C, because only the mineralogical phases in WNL could remain after cement calcination.

**Table 3**
Proportion scheme of cement raw meal and WNL residue (wt.%).

| Samples | Raw meal | WNL residue |
|---|---|---|
| A | 100 | 0 |
| B | 99.85 | 0.15 |
| C | 99.7 | 0.3 |
| D | 99.55 | 0.45 |

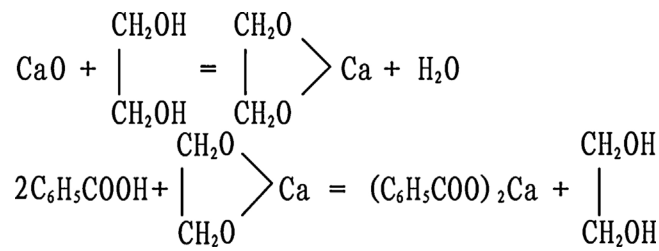

**Fig. 1.** The reactions of CaO during titration.

The powder samples were well mixed, and the sintering temperature was set at 1300, 1350, 1400 and 1450 °C in an electrical furnace. After sintering the samples were cooled rapidly, ground into powder and filtered with a #180 mesh (with 80 μm pore diameter) sieve. The samples acquired at 1450 °C were chosen to be characterized to demonstrate the qualities of cement clinker.

### 2.3. Principles and methods

WNL residue used for calorific value measurement was obtained at 150 °C, in order to keep the organic component as much as possible. The oxygen bomb calorimeter was employed. The actual calorific value of WNL was calculated accordingly.

The setting time of acquired cement clinker, which could be used to characterize the solidification speed, was tested according to the Chinese National Standard *GB/T 1346-2001* [27]. The strength of mortar made from produced cement clinker was tested according to the Chinese National Standard *GB/T 17671-1999* [28].

After calcination, the unreacted CaO in clinker is called free lime, or $f_{CaO}$ for short. It can react with ethylene glycol ($C_2H_6O_2$) in anhydrous ethanol solution at 100–110 °C, forming ethylene glycol calcium, shown as the first reaction in Fig. 1, which can make the indicator phenolphthalein turn red. And the anhydrous ethanol solution of benzoic acid ($C_6H_5COOH$) could be utilized to titrate it, making it go back to colorless, shown as the second reaction in Fig. 1. The titration reactions could be employed to quantify the $f_{CaO}$ content, and then to analyze the burnability of cement raw meal accordingly. The titration tests were carried out according to the Chinese National Standard *JC/T 735-2005* [29] and *GB/T 176-2008* [30].

## 3. Result and discussion

### 3.1. Characterization of raw materials

After being calcinated at 150, 250, 350, 450 and 550 °C, the WNL turned to yellow residue in solid state. And the residues were weighed; the mass loss ratios were 27.3%, 50.9%, 51.3%, 52.2% and 52.8%, respectively.

When calcinated at 150 °C, the mass loss could be approximately considered as the vaporization of water, which was 27.3%. When it reached about 52%, the mass loss ratio almost remained the same. It could be considered that, all kinds of water (including free water and bound water) and most of organics would decompose and escape from WNL at 550 °C, which means the solid mineralogical phases in WNL occupy about 48% by weight.