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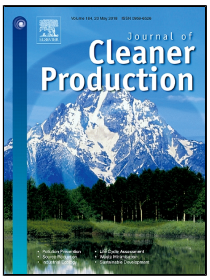

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New advancement perspectives of chloride additives on enhanced heavy metals removal and phosphorus fixation during thermal processing of sewage sludge

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Highlights

1. The behavior of phosphorus and heavy metals during thermal processing was studied.
2. 81.6% of Cu and 96% of Pb can be removed from sewage sludge ash.
3. The removal efficiency of heavy metals and the Phosphate fixation were studied.
4. Sewage sludge was calcined with an inorganic chlorinating agent MgCl2 and KCl.
5. High temperatures promote the transformation of P from NAIP to AP

Abstract

Controlling the removal of heavy metals such as Copper (Cu), Zinc (Zn), lead (Pb) and cadmium (Cd) during the sewage sludge incineration and the recovery of phosphorus (P) from sewage sludge ash (SSA) remain challenging. Herein we aim to investigate the effect of the temperature, retention time and chlorinating agent additives ($MgCl_2$ and KCl) on both the behavior of selected heavy metals and the fixed rate of phosphorus (P) during sewage sludge incineration. Dry sewage sludge was mixed with various amounts of chlorinating agent and treated by a laboratory scale furnace in the temperature range of 800-1000^{o}C for different retention times (30, 60 and 120 minutes). The results demonstrated that the removal efficiency of heavy metals exhibited an increasing tendency with the addition of chloride, especially in the cases of Cu, Zn and Pb. Moreover, the temperature and retention time demonstrated significant effects on the promotion of heavy metals removal. In the case of Pb 96% was removed at 800^{o}C within 120 minutes, while 86.6% of Cd was effectively removed at 1000^{o}C within 30 minutes. $MgCl_2$ proved to be more effective than KCl in improving the removal efficiency of heavy metals, such that up to 81.6% of Cu, 84.9% of Pb and 73.5% of Zn was removed with the addition of 15%wt Cl^-/sewage sludge (SS), At 960^{o}C, the boiling point of cadmium chloride $CdCl_2$ and $CdO.Al_2O_3.2SiO_2$ retention time and chlorinating agent had no impact on Cd removal. It was also observed that high temperature was beneficial for the transformation of non-apatite inorganic phosphorus (NAIP) to apatite phosphorus (AP). At 900^{o}C this transformation is efficient for Phosphate fixation, which is evidence that apatite phosphorus (AP) has the ability to be more stable than non-apatite inorganic phosphorus (NAIP) at high temperature.

Keywords: Sewage sludge; Heavy metals; Phosphorus; Thermal treatments; Removal efficiency

1. Introduction

Phosphorus is a restricted resource, and is essential as a major nutrient for the growth of life in most ecosystems. Phosphorus can't be replaced by other elements and, it is an important element for many manufacturing processes as well (Biswas et al., 2009). The consumption of phosphorus fertilizer increased from 9×10^6 to 40×10^6 metric tons between 1960 and 2000 with the increase in the world's population and was predicted to increase further to 200×10^6 metric tons by 2030 (Tilman et al., 2001).

Sewage sludge (SS) ash has considerable potential to be used as a minor source of phosphate for the production of fertilizers and phosphoric acid (Speir et al., 2007). Previous studies have revealed that in China the annual discharge of ewage sludge (80% water ratio) is to be more than 20 million ton in 2013 (Dai et al., 2013). Currently, more than 16 million ton of sewage sludge was discharged to the environment without treatment, resulting in serious environmental pollution. It is therefore urgent that effective measures to deal with sewage sludge in China are developed and implemented (Duan et al., 2012).

Related study about sewage sludge incineration has revealed that after the organic contaminants and pathogens are completely destroyed, 60–70% of the phosphate is fixed in the sewage sludge ash. Compared to phosphorous ore which reaches 26%, the P_2O_5 content of sewage sludge ash has been found to be 15%, equivalent to the lowest levels in phosphate rock (Coutand et al., 2008). According to Schipper et al., 2004, bottom ash contains considerable amounts of phosphorus at about 16% P_2O_5. In China, the average phosphorus content in sewage sludge is 22g P/kg SS, with the maximum reaching 37g P/kg dry solids SS. Therefore, the recovery of the phosphorus from the bottom ash for use in the phosphate industry is possible and needed (Guo et al., 2009).

Sewage sludge contains large amounts of inorganic mineral matter rich in nutrients (N, P, K, etc.), however, sludge containing odorous substances, pathogens, persistent organic compounds and heavy metals, has the potential for grave harm to the environment (Coutand et al., 2008; Rasković, 2007). It contributes to contaminated land, smelly, polluted groundwater and rivers and lakes. Specifically, sludges containing heavy metals and other toxic substances which cannot be decomposed bymicroorganisms pose the greatest risk (Rio et al., 2007). Landfill and agricultural utilization are unsustainable approaches to sludge management due to the excess of sewage sludge production and the high concentration of heavy metals in sludge (Donatello and Cheeseman, 2013). A study by Smith (2009) indicated that heavy metals and some toxic organisms in landfilled sewage sludge can be absorbed by agricultural plants in concentrations that are potentially hazardous to the human food chain.

Recently one of the main technologies for the treatment of sewage sludge to obtain useful products is a thermal process (Otero et al., 2002). Incineration of sewage sludge has special advantages such as volume reduction, destruction of organic pollutants and energy recovery, in contrast with landfill and agricultural utilization (Wang et al., 2005). Sewage sludge ash encloses inorganic components such as Al_2O_3, SiO_2, and flux (e.g. Fe_2O_3, CaO, MgO) as shown in Table.2 (Adam et al., 2009; Monzó et al., 2003).

Related study has demonstrated that CaO additives can increase the phosphorous and heavy metals during incineration of sewage sludge, while with HCl additives the amounts of phosphorous and heavy metals decreased in the bottom ash (Han et al., 2009). Substantial amounts of heavy metals occur in sewage sludge ash, especially Zn, Cu, Pb, and Cd, more easily vaporized than P (2001; Hultman and Löwén, 2001). Hence, capture of these elements prior to or during the incineration process is a priority.

Heavy metal chlorides are of interest because of their high vapour pressure. The condensation process of these heavy metal compounds can be delayed during thermal treatment. This condition accelerates the removal efficiency of heavy metals from the sewage sludge and its ash. Thus, sewage sludge can be mixed with a desired quantity of Cl^- agent for effectively separating heavy metals from sewage sludge ash, that is, the reaction mechanism of the chlorinating agent (such as $MgCl_2$ and KCl) promotes the effective separation of heavy metals (Nowak et al., 2012), according to reactions 3.1 to 3.4.

Previous work by Maroušek et al., 2015 demonstrated that the solid residue of pyrolysis (biochar) represents a more attractive product. Biochar has a high adsorption capacity that can reduce the bioavailability of some heavy metals and organic pollutants (Maroušek et al., 2017). Extensive investigation on heavy metals in solid waste incineration ash (SWIA) has generally concentrated on solidification and stabilization (Nowak et al., 2012). Thermal isolation technology of heavy metals principally exists in MSWI fly ash, but seldom in sewage sludge ash (Speir et al., 2007). In the present work, sewage sludge was incinerated at 800^{o}C with various additive mass ratios (5% to 15% of $MgCl_2$, also with 15% of KCl separately) and a retention time of 60 minutes. From the results, we found that $MgCl_2$ is more effective for most heavy metals removal than KCl as shown in Fig.7. The heavy metals contents (Cu, Zn, Pb, and Cd) in dried sewage sludge ash showed the tendency to decrease with increased amounts of $MgCl_2$, chlorinating additives. This phenomenon was significantly clear for Cu, Pb and Zn heavy metals.

The effect of retention time during sewage sludge incineration on the efficiency of heavy metals removal has not been studied. Therefore, the aim of this study was to estimate and compare the influence of the operating parameters temperature, retention

time and chlorinating agent on the removal efficiency of heavy metals and on the fixation of phosphorus in the incinerated sewage sludge. Moreover, the reaction products resulting from chemical stabilization of phosphorous in sewage sludge at different temperature levels (800,900 and 1000^{o}C) are also studied.

2. Materials and methods

2.1. Materials

Sewage sludge used in this study, was collected from a wastewater treatment plant (WWTP) located in Dalian city, Liaoning province, China. The samples used in this work were obtained from the top 15 cm stratum of the sampling sites at a distance of at least 20 meters from a wastewater treatment plant. The sewage sludge was stabilized by anaerobic digestion for 72 hours, followed by drying in an electric oven at 105°C for 12 hours. The average water content of the samples was 79%. Dried sewage sludge sample was mixed with the desired amount of chlorinating agents KCl and $MgCl_2$ separately and then placed in a laboratory scale furnace, where it was burned for 1h at 800°C. Crushed and sieved with 120μm meshes, the chloride used in the experiment was technical grade (with a purity of more than 98%, content of magnesium and alkali is less than 2%) supplied by Sinopharm Chemical Reagent Co., Ltd. China. The properties of the sludge are listed in Table.1. X-ray fluorescence (XRF) was applied to detect the chemical compositions of the dried sewage sludge (DSS). The results obtained are presented in Table.2. The mass fractions of heavy metals and phosphorus in dried sewage sludge at 105^{o}C are given in Table.3. The technical path of the experiments and the design of Dalian WWTP are shown in Fig.1 and Fig.2.1.

2.1.1. Preparation of ascorbic acid 10%

10g of 10% ascorbic acid was dissolved in deionized water in a 100mL volumetric flask within the volume made up to 100mL with deionized water. The preparation of the ascorbic acid solutions was done immediately before use as ascorbic acid solutions are not stable for a long time at room temperature. Standard stock solutions were prepared from anhydrous K_2HPO_4 (Suprapur, Merck). The reagents used for the phosphate detection were all Suprapur (Merck) quality. All solutions were digested by double-deionized water (USF Purelab Plus 18.3 μS cm^{-1} resistivity). Laboratory reagent grade 37% hydrochloric acid and 98% sulphuric acid as well as nitric acid (65%), and perchloric acid (70%) were used in the digestion procedure.

2.1.2. Molybdate solution

A- Ammonium molybdate: 13g of Ammonium heptamolybdate, $(NH_4)_6MO_7O_{24}$ $4H_2O$ was dissolved in 100mL volumetric flask with deionized water and completed to the volume with the same solvent.

B- 0.35g of $((K(SbO)C_4H_4O_6))$ was dissolved in deionized water and made up to 100mL with deionized water.

C- 300 mLHCl 1:1 solution

The previous three solutions (A, B, and C) were mixed together to make the molybdate solution**.**

2.2. Experimental apparatus

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Perkin Elmer Optima 8300) was used to detect heavy metals contents in the calculated sewage

sludge ash samples after digestion by HNO_3, HF, and $HClO_4$ solutions, and incineration on the laboratory-scale tube furnace (length: 1100 mm, inner diameter: approximately 75 mm). X-ray fluorescence (XRF Rigaku ZSX100e) was used to measure the specific surface area and detect the main elements in SSA. Agglomeration on the SSA used was observed by field emission scanning electron microscopy (SEM, FEI Nova NanoSEM 450). The major crystalline compounds in SSA were detected by X-ray diffraction (XRD, PANalytical X'Pert PRO). The molybdenum blue method was used to detect the different Phosphorus fractions in all the extracts by spectrophotometer (WFJ2100, UNICO, China).

Simultaneous thermal analysis was carried out in a Netzsch STA 449F3 instrument, which was utilized in the thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) configuration with samples and reference crucibles made of Al_2O_3. Powder samples were mixed well (10g, particle size <120μm) and were placed in a porcelain crucible, which was placed in a heavy aluminium tube. An air rate of 0.2 m^3/h was maintained while the tube furnace chamber temperature was at 800-1000^{o}C for 30-120 min.

2.3. Experimental analysis methods

2.3.1. Digestion process

To prove the removal efficiency of heavy metals during incineration process, 5.00g of sewage sludge with and without added chlorides agent was placed in a laboratory-scale furnace and incinerated at temperatures of 800-1000^{o}C for a specific time (30, 60 and 120min).The remaining SSA was milled and sieved to less than 120μm for digestion with a mixture of HNO_3, HF, and $HClO_4$ (Calvo et al., 2004).

The protocol applied was as follows: a well-mixed sample of 1.00±0.001g SSA was weighed and placed in a porcelain crucible (20mL). HNO_3 was added, and the solution was heated for 2h at 190±10°Cand cooled. 10mL of HF was then added and heating continued for 2h, followed by cooling once again. The process was repeated with 10mL $HClO_4$ until approximately no liquid was left. Then 3mL $HClO_4$ was added. Heating at 190±10°C was applied until the remaining material was nearly dry and either grey or white. Then, 25mL of 2% HNO_3 added to the residue. Finally, the filter liquor was moved into a volumetric flask and diluted to 50mL with deionized water. Measurements were taken by ICP-OES to determine the concentrations of selected heavy metals (Cu, Zn, Pb, and Cd). Three replicates were used for the analyses. Total Phosphorous was detected by using the Standards Measurements and Testing (SMT) Program of Europe (He et al., 2003).

2.3.2. Thermal Characteristics

The thermal behaviours of samples were carried out by thermogravimetric analysis (TGA-DS). A Netzsch STA449F3 instrument was used to illustrate the TG-DSC results of sewage sludge behavior during incineration process as shown in Fig.2. The crucibles used for both reference and samples made of Al_2O_3 in (DSC) Configuration. Before starting the experiments, temperature, weight, and sensitivity calibrations of the instrument were conducted using calibration sets provided by Netzsch. The purge gas was air using a flow rate of 50mL/min, and the sample was heated from 10°C to 1200°C at a heating ratio of 10°C/min. 4-10mg of the Samples were weighed and placed into a Pt-Rh crucible with 20 taps. All curves were estimated by the TA-instruments software.

2.3.3. SMT Methodology

Protocol was originally planned to acquire five fractions of P See Fig.2.3.

3. Results and discussion

3.1. SEM analysis

Dalian sewage sludge bottom ash morphology at 800, 900 and 1000^{o}C for retention time 60min with and without chlorinating agent are presented in Fig.3a-d. SEM was visualized to prove the dissimilarities in the microstructure for dried sewage sludge before and after adding chlorine additives. As shown in Fig.3a the micro appearance of sewage sludge ash at 800^{o}C shows the existence of floc-like material, this is supposed to be the crystal particle of heavy metal substances and CaO. The untreated SSA exhibits irregular mineral crystal grain see Fig.3a-c, the heavy metals and CaO crystals which are supposed to be the apatite-like mineral phase matching to $Ca_8Pb_2(PO_4)_6(OH)_2$ and $Ca_{18}Cu_3(PO_4)_{14}$ peaks in the XRD graph Fig.4b. The micro appearance of the SSA particle illustrates respectable changes by melting and sintering which occur during incineration at 800, 900 and 1000^{o}C for 60min retention time, as shown in Fig.3a-d. The holes missing and the surface completely turns into downy and thick after adding chlorinating agents, which proves the heavy metals removal (Cu, Zn, Cd, and Pb) from sewage sludge ash after adding chlorinating agents. As shown in Fig.3d adding Cl^- species the slushy and vitreous substances on the spot surfaces were absent, and the surface changes to an angular shape, this sewage sludge ash consists of alumina silicates and phosphate ores as illustrated in Fig.3d.

Heavy metal phosphate compounds, such as $3CuK_2(PO_3)_4$, $CdSiP_2$, $Pb_2(P_2O_5)$ and $Zn_3(PO_4)_2$ were detected with absence of chlorinating agent in the dried sewage sludge

ash were not detected after adding Cl^- agent, this is very beneficial to the environment and provides practical ways for recycling phosphate from SSA.

3.2. X-ray diffraction analysis

The crystalline phase of SSA before and after calcination are presented in Fig.4.a,b. The main crystalline phase of the bottom sewage sludge ash at 800°C-1000°C is SiO_2 ,$AlPO_4$, and P_2O_5. As shown in Fig.4.b, the peak strength for $AlPO_4$ clearly increases at 1000°C, while the changes for SiO_2 were not obvious. At 900°C the silicate products such as $CdSiP_2$ have been proved in sewage sludge ash. The strength of MP_2O_5 peaks are decreased at higher temperatures, which proved the high influence of temperature on the removal efficiency of heavy metals and phosphate fixation.

As shown in Fig.4.b. The ash from sewage sludge contains ferrates (e.g., Fe_2O_3), aluminium silicates (e.g., $KAlSi_3O_8$), and phosphates (e.g.,Ca_9 (Fe, Al) $(PO_4)_7$ and Ca_4 (Mg, Fe)$_5(PO_4)_6$), Phosphorus in the sewage sludge ash occur as phosphorus compounds in the forms of K_3Al_2 $(PO_4)_2$ and Ca_4 $(Mg_3Ca_{3)}$ $(PO_4)_4$, these phosphorus compounds are supposed to be derived from MP_2O_7 where there are five metals locations (M1−M5) and three phosphorus places available (P1−P3) in the structure and the metal positions M4, and M5 can either be occupied-unoccupied, or partly occupied by elements Like Fe, Al, and Mg. Fig.4.a, demonstrated that the crystalline phases of the mixture ash are dissimilar for single sample ash with the other samples that included chloride additives, because of the combined interactions between the volatile elements such as K in sewage sludge ash with chloride additives, the main ash induce the formation of Al, Si, Ca, and P.

The phosphate content in the residual ash increases significantly after adding the chlorides agent, owing to the bond between aluminium silicate minerals $P_2Al_3Si_2O_6$,

$K_3Al_2(PO_4)_2$ and phosphates ($Mg_3Ca_2(PO_4)_4$, which mostly exist in the K−Al−Si and K−Ca−P triangular systems. An evident mechanism between $Mg_3(PO_4)_4$ and alkali metals has not been established yet. Thus, $Mg_3(PO_4)_4$ is selected as the phosphorus-containing model compound in sewage sludge ash to detect the mechanism of the reaction between chloride additives and the phosphorus in sewage sludge ash. As shown in Fig.3, the formation of irregular mineral crystal grain that covers the $Mg_3Ca_3(PO_4)_4$ crystal, which is supposed to be the apatite mineral phase $Ca_8Pb_2(PO_4)_6(OH)_2$ and $Ca_{18}Cu_3(PO_4)_{14}$.

3.3. Behaviour of heavy metals and Phosphorus during thermal process

The DTG-DSC curves of the sludge combustion are shown in Fig.2. The DTG-DSC curves for sewage sludge ash without additives can be devided into four stages. Drying stage occurs below 100°C. The second stage, low-temperature stage happens in the range of 200–350°C and double peaks are detected, while the first peak results presumably from the decomposition of undigested organics and dead bacteria, the second peak is due to the volatilization of organic polymers. The third stage, the medium temperature area begins after the low-temperature state between 350 and 550°C, the char combustion is supposed to take place at this stage. The fourth stage occurs above 550°C, where rapid oxidation of the stayed volatile matter in the SS is occurred without identifying any peak of DTG. This process results in the loss of weight due to the volatilization of char and the non-degradable compounds such as cellulose substantial.

According to the SMT Protocol OP is converted completely to IP at 450°C. TP was calculated as the sum of NAIP and AP, the results are presented as mean values

(expressed in $mg.g^{-1}$) and standard deviations. As shown in Fig.6, the content of TP clearly increased in the temperature range between 800–900°C and reached a maximum value of 89.91$mg.g^{-1}$ at 900°C. Results revealed that IP has slightly increased between 800–900°C and no obvious changes at 1000°C. The content of NAIP clearly increased, and for AP there is no significant change at 800°C and 1000°C the obvious changes appears at 900°C. At the same time, the transformation from NAIP to AP is efficient for Phosphate fixation, which evidence that AP has the ability to be stable than NAIP at high temperature see Fig.6.

3.4. Retention Proportion of Heavy Metals in SSA

The correlation between the different temperature level and removal rate of Cu, Zn, Pb and Cd within 60min retention time (RT) shown in Fig.9. The fractions of heavy metals residual in sewage sludge ash after incineration process with and without chlorinating agent additives ($MgCl_2$ and KCl) is defined as it follows, (R) refers to retention ratio of heavy metal which was calculated by the following equation.

$$R = \frac{C_A M_1}{M_0 C_S} \times 100\% \qquad \text{(Eq.1)}$$

Where:

D- $\boldsymbol{M_1}$*:* Refers to the weight of SSA g

E- $\boldsymbol{C_S}$*:* Refers to the heavy metal amount in the initial SS mg/kg

F- ***R****:* Refers to the Ratio of heavy metals in SSA

G- $\boldsymbol{C_A}$*:* Refers to heavy metal amount in SSA, mg/kg

H- $\boldsymbol{M_0}$: Refers to the initial weight of the sewage sludge in g

Mass fractions of Cu, Zn, Pb, and Cd at 800, 900 and 1000^{o}C are listed in Table.4. As shown in Fig.5, removal efficiency of heavy metals (Cu, Zn, Pb, and Cd) is clearly improved when we increased the temperature. These heavy metal removals were greatly increased to 20.4%Cu, 49.9% Zn, 63.8% Pb and 86.6% Cd, respectively, under the conditions of 1000^{o}C and 60min retention time without addition of chlorinating agent. The obtained results revealed that the high influence for temperature was for Cd, this phenomenon supporting the results obtained for the boiling points of Cd compounds 960^{o}C.

The Cu, Zn, and Pb removal ratio was positively associated with the amount of chloride addition, and the highest removal efficiency appeared under the addition condition 15%wt Cl^- /SS. As shown in Fig.7, the highest removal efficiency achieved was for Cu, Zn and Pb, for Cd removals was not significant, 84.9%, 81.6%, and 73.5% of Pb, Cu, and Zn were removed respectively and only 29% of Cd was removed under the conditions of 800^{o}C, 15%wt Cl^-/SS within 60min retention time. Retention time had positive influences on the removal of heavy metals in the order of Pb > Cu > Cd > Zn when the retention time increased to 120min at 800^{o}C without any addition of Cl^- the heavy metal removals were increased by the percentage 96%,63.8%, 22.2% and 11.8% respectively for Pb, Cu, Cd and Zn as shown in Fig.9.

3.5. Factors affecting heavy metals removal

3.5.1. Different added amounts of chlorinating agent

When 15% wt of Cl^-/SS was added, the contents of Cu, Zn and Pb was reduced from 13360 mg/kg.SS, 6410 mg/kg.SS and 132.75 mg/kg.SS to 2500 mg/kg.SS, 1700 mg/kg.SS and 20 mg/kg.SS respectively after adding chloride. This indicate that the addition of $MgCl_2$ 15% wt of Cl^- improves the removal efficiency of Cu at 800^{o}C within

60min RT to reach 81.6% more than of that without adding Cl^-, the removal efficiency of Zn was approximately 73.5% more than of that without chlorinating agent addition under the same condition. While the removal of Cd and Pb was approximately 29% and 84.9% respectively higher than of that without chlorinating agent as shown in Table.5. When the addition ratio of $MgCl_2$ was 5% Cl^- to the sewage sludge, the removal efficiency of Cu, Zn, Pb and Cd was 53.5%, 51.6%, 69.9% and 18.7% respictivly. In this case, the difference in the heavy metals removal promoting effect is easily visualized, according to the order: Pb>Cu >Zn> Cd. While, the removal efficiency of Cu, Zn and Pb heavy metals in sewage sludge ash was increased to 59.4%, 67.2%, 54.5% respectively, after using15% of KCl, only 14.3% of Cd was removed.

Comparing KCl and $MgCl_2$ as Cl^- sources for heavy metal migration impact, $MgCl_2$ has more significant effect. From Fig.7, we can see that, increasing the proportion of $MgCl_2$ the residue of selected heavy metals, Zn, Cu, Pb and Cd tends to decrease. The most obvious changes were observed for Cu, Pb, Zn, which follow the following mechanism reactions:

$$Mg + 1/2O_2 \rightarrow MgO + Cl_2 \quad (3.1)$$

$$CuO + Cl_2 \rightarrow CuCl_2 + 1/2O_2 \quad (3.2)$$

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

$$CuO + 2HCl \rightarrow CuCl_2 + H_2O \quad (3.3)$$

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \quad (3.4)$$

$$CdO + Al_2O_3 \bullet 2SiO_2 \rightarrow CdO \bullet Al_2O_3 \bullet 2SiO_2$$

The product of the reaction $CdO.Al_2O_3.2SiO_2$ was very stable so that the calcination process for sewage sludge for the promotion-removal of Cd heavy metal was not ideal. For Cu, Zn, and Pb, heavy metals with $MgCl_2$ promote its volatile characteristics more effective than that with KCl, according to the obtained results when the addition ratio of Cl^- was between 5-15%, the removal efficiency of heavy metals Cu, Zn, and Pb have a positive correlation with Cl^- agent.

3.5.2 Retention time

Fig.9, illustrates the impact of the retention time on the removal efficiency of heavy metals, the result proved that the retention time has significant effects on the removal rate of Pb and Cu as shown in Fig.9, the removed ratio of Cu reach to 64.8% at 120 min and the highest influence was for Pb, 96.0% was removed of lead (Pb) when the retention time increased from 30min to 120min. Table.6 included the heavy metals content in SSA at 800^{o}C and retention time between 30-120min. Among all selected elements the highest influence of the retention time was on Pb followed by Cu. There was a slight effect of the retention time for the removal of Zn and Cd, only 11.8% and 22.2% were removal respectively. Regarding the boiling points of $CdO.Al_2O_3.2SiO_2$ and $CdCl_2$ chlorides, which is 960^{o}C there were no clear effects for the retention time and chlorinating agent on the Cd removal.

4. Conclusions

The influence of chlorine, temperature and retention time on heavy metals removal efficiency from SSA was investigated. In general, their removal found to be chlorine dependent, especially for Cu, Pb and Zn. In this case, the temperature was appropriate to promote the removal efficiency of heavy metals to some extent. During sewage sludge incineration, increasing the retention time improved significantly the

removal efficiency of heavy metals in SSA, this was obvious in the case of lead, which showed 96.0% of the removal after 120min retention time at 800^{o}C without adding any chlorinating agent. As shown in Fig.8, comparing the different parameters that were involved in the removal efficiency of heavy metals their removal efficiency was as follows: Chlorinating agent > Temperature >Retention time.

Chlorinating agents exhibits an obvious influence on the heavy metal removal, especially for the Pb, Cu and Zn, which show a total removal of 84.9%, 81.6% and 73.5%, respectively, and only 29% of Cd can be removed from SSA with $MgCl_2$ 15%wt Cl^-/SS. During the sewage sludge incineration, all the selected heavy metals Cu, Pb and Zn were positively correlated with $MgCl_2$, except for Cd, which exhibits a removal below 30%. The formation of CdO_4^{2-} decreases the Cd removal efficiency after adding $MgCl_2$, in addition to the formation of ($MgAl_2O_4$) compound, which minimizes the influences of Cl^- on Cd removal. Moreover, sewage sludge incineration temperature exhibits an obvious influence on phosphate fixation and transformation. Indeed, the total phosphorus (TP) content in treated sewage sludge ash increases from 85.12 mg/g SS at 800^{o}C to 89.91 mg/g SS at 900^{o}C, in addition to its positive effect on the transformation of NAIP to AP at 900^{o}C, in this case more than 50% of NAIP is transformed to AP at 900^{o}C and changed remains significant at 1000^{o}C. The transformation from NAIP to AP is efficient for Phosphate fixation, which indicates that the AP is prone to be stable than NAIP at high temperature as shown in Fig.6. The main mineral phases of AP were $Ca_8Pb_2(PO_4)_6(OH)_2$ and $Ca_{18}Cu_3(PO_4)_{14}$ which were detected by XRD and SEM. Moreover, the main components are essentially phosphate ores. Therefore, the goal of the work reported herein is to improve both the heavy metals removal and the fixation of phosphate during the sewage sludge incineration,

which provides environmental benefits and paves the way for the development of effective methods for sewage sludge recycling.

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Table.1. Immediate and final analysis of dried SS at 105^{o}C (wt%).

Table.2. Major chemical components of dried SS at 105^{o}C (wt%).

Table.3. Phosphorus and heavy metals mass fractions in dried sewage sludge at 105^{o}C (mg.g^{-1}).

Table.4. Mass fractions of HM in sewage sludge ash at temperature between 800 - 1000^{o}C within 60 minutes retention time (mg.kg^{-1}) SSA.

Table.5. Mass fractions of HM's in sewage sludge ash with different amounts of Cl^- additives at 800^{o}C and 60 minutes retention time (mg.kg^{-1}) SSA.

Table.6. Heavy metals concentration in SSA at 800^{o}C and different retention time (mg.kg^{-1}) SSA.

Table.7.Mass fractions of phosphorus at different temperature and 60 minutes retention time (mg.g^{-1}) SSA.

Fig.1. Technical path of the experiments.

Fig.2. Illustrate TG-DSC results of sewage sludge without Chloride agent.

Fig.2.1. Design and processing parameters of Dalian WWTP.

Fig.2.3. Operating situations in the SMT extraction protocol.

Fig.3. SEM was used to study the Surface properties of Incinerated Sewage sludge ash before and after calcination with 15%KCl at (800 -1000^{o}C) with RT 60 minutes.

(A,B) At 800^{o}C and 900^{o}C for 60 minutes without Cl^{-} additives.

(C) At 1000^{o}C for 60 minutes without Cl^{-} additives.

(D) At 800^{o}C after calcination with 15% Cl^{-} as KCl and 60 minutes RT.

Fig.4. X-ray diffraction model of the sewage sludge ash at (800-1000^{o}C).

(A) With Cl^{-}.

(B) Without Cl^{-} additives.

Fig.5.The effects of temperature on heavy metals removal in SSA within 60min retention time.

Fig.6. P mass fractions in sewage sludge ash at different temperatures within 60minutes retention time (mg.g^{-1}) SSA.

Fig.7. The effects of chlorinating agent on removal efficiency of heavy metals during SSI at 800^{o}C and 60 minutes retention time (mg.kg^{-1}SSA).

Fig.8. Comparison of the applied parameters on the removal efficiency of heavy metals during sewage sludge incineration (%).

Fig.9. The effects of retention time on heavy metals removal efficiency during SSI at 800^{o}C (%).

Nomenclature

(SSA) Sewage Sludge Ash

(SS) Sewage Sludge

(NAIP) Non-apatite Inorganic Phosphorus

(AP) Apatite Phosphorus

(MSWI) Municipal Solid Waste Incineration

(WWTP) Wastewater Treatment Plant

(TGA) Thermo Gravimetric Analysis

(DSC) Differential Scanning Calorimetric

(SEM) Emission Scanning Electron Microscopy

(XRD) X-ray Diffraction

(XRF) X-ray Fluorescence

(DSS) Dried Sewage Sludge

(RT) Retention Time

(ICP-OES) Inductively Coupled Plasma-Optical Emission Spectrometry

Figures

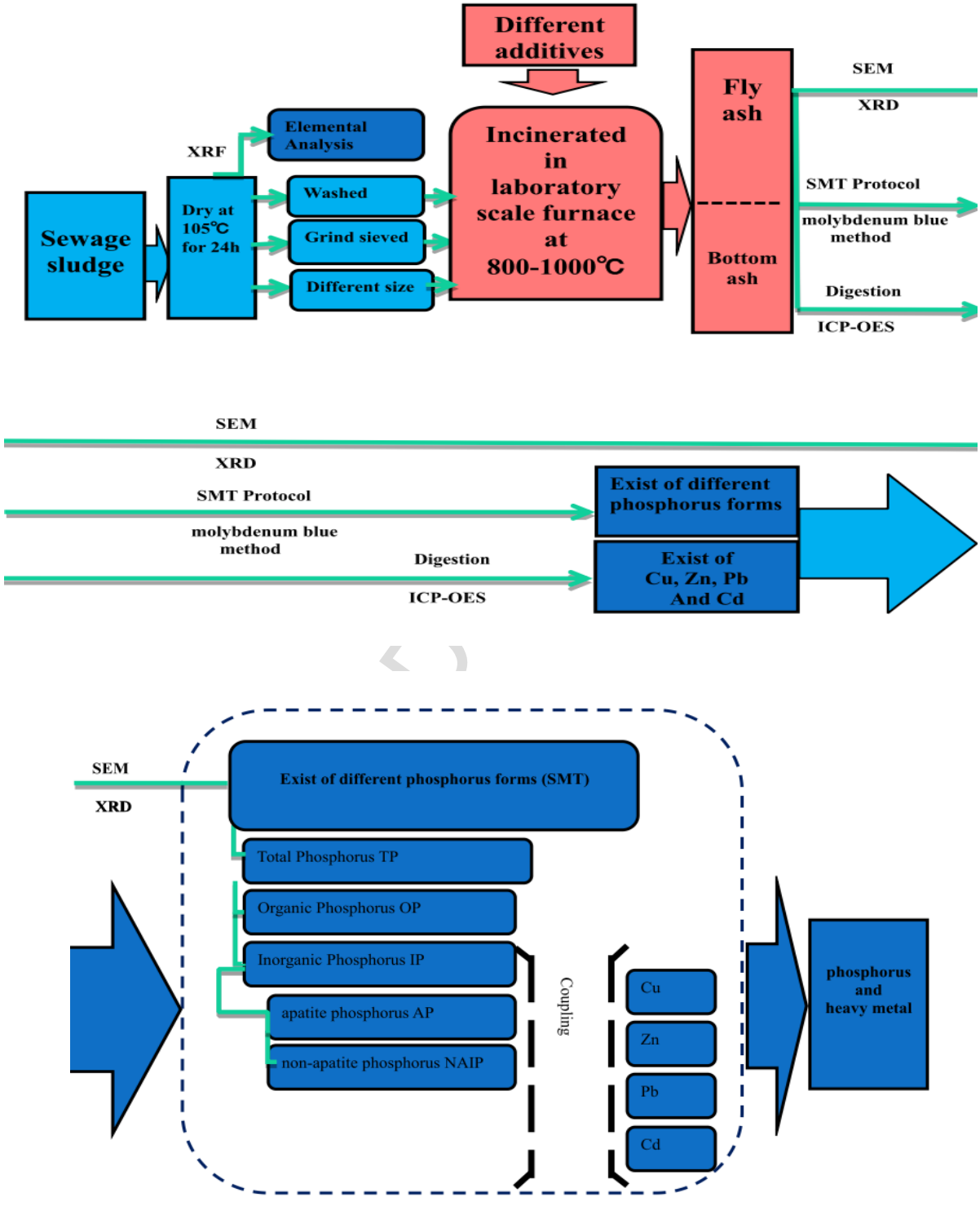


Fig.1. Technical path of the experiments.

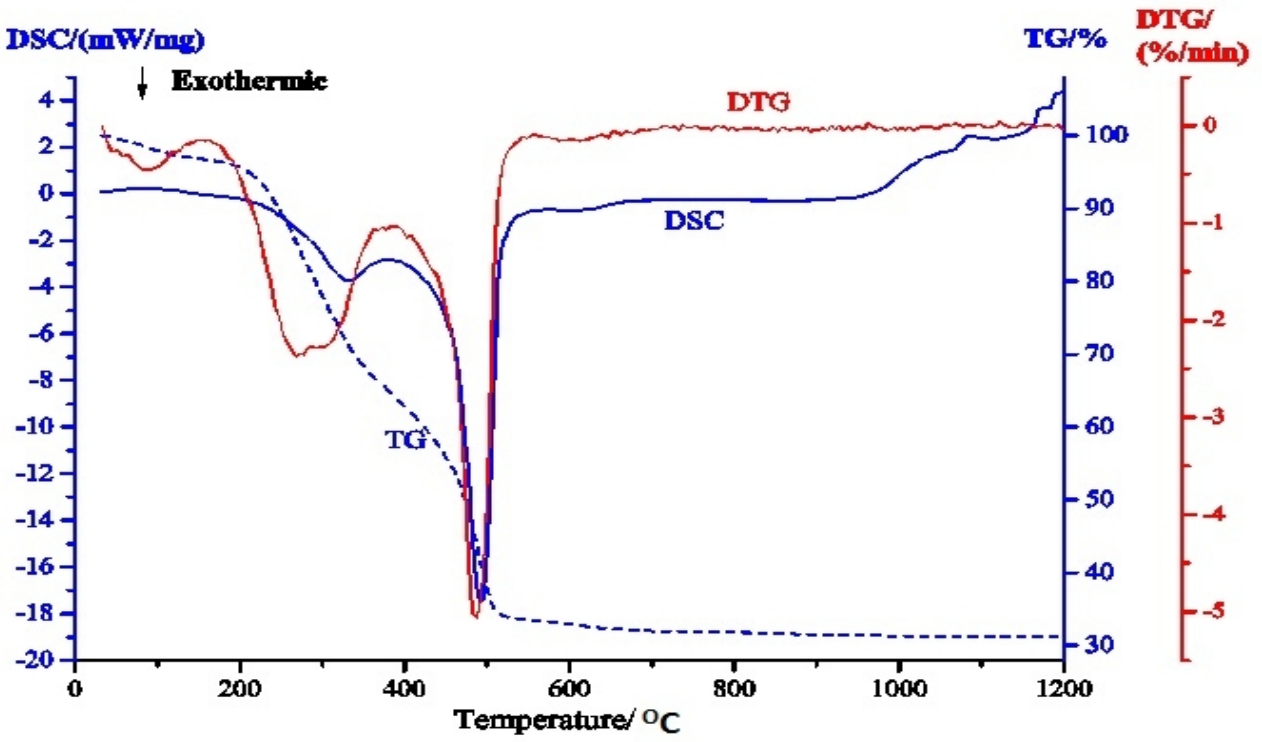


Fig.2. Illustrate TG-DSC results of sewage sludge without Chloride agent.

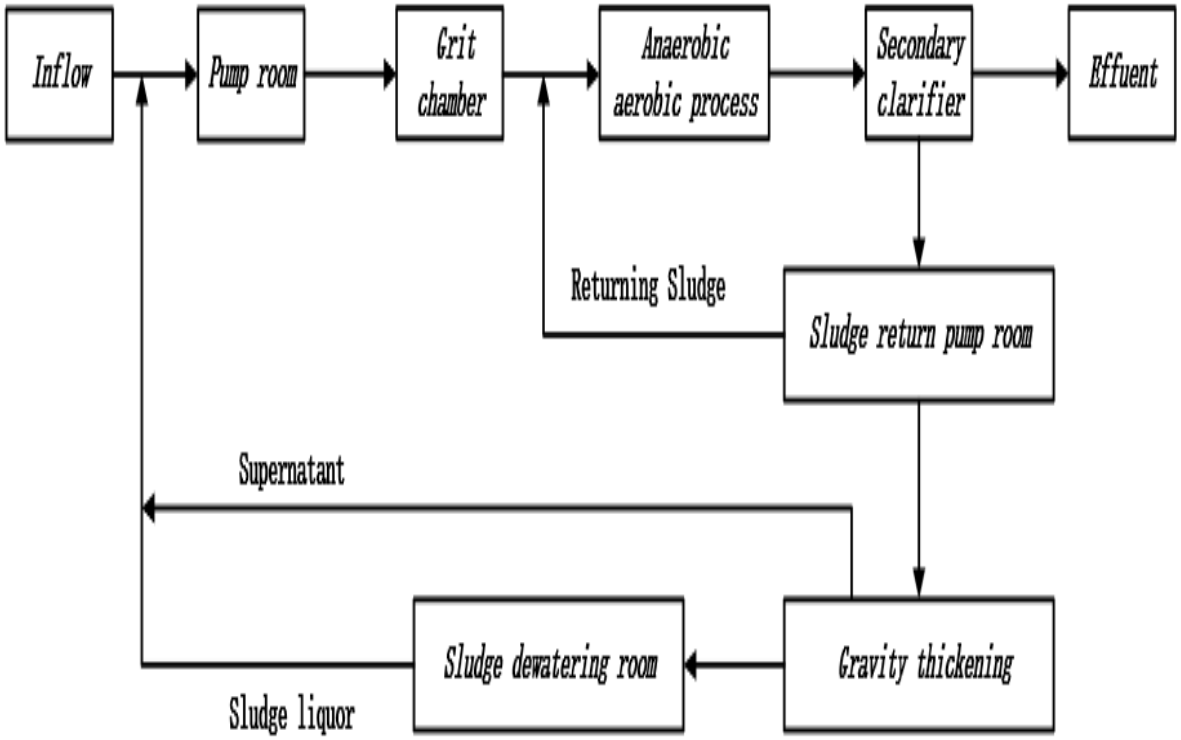


Fig.2.1.Design and processing parameters of Dalian WWTP.

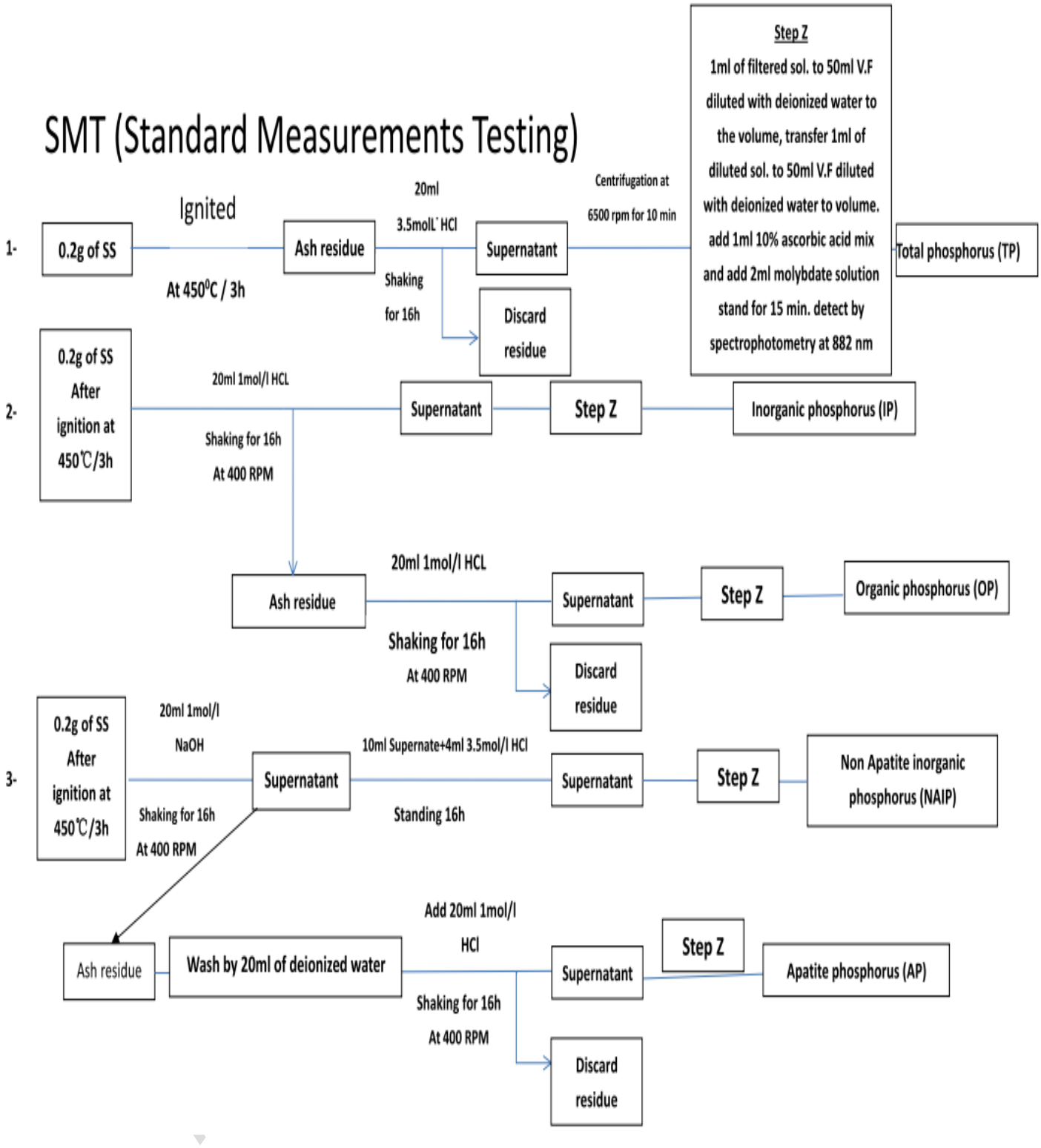
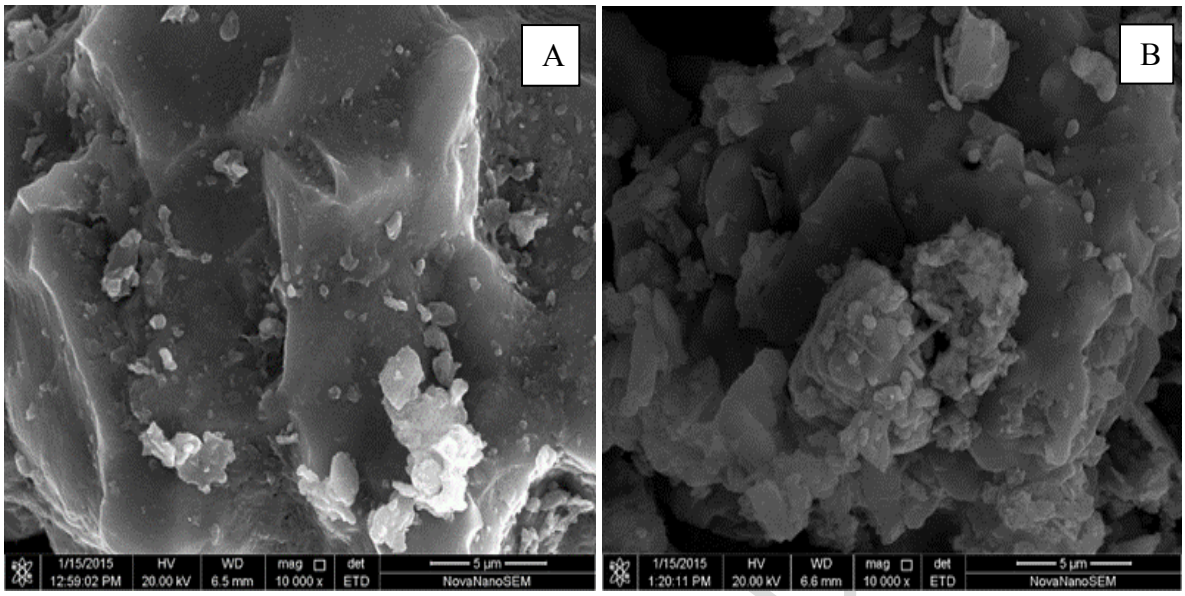
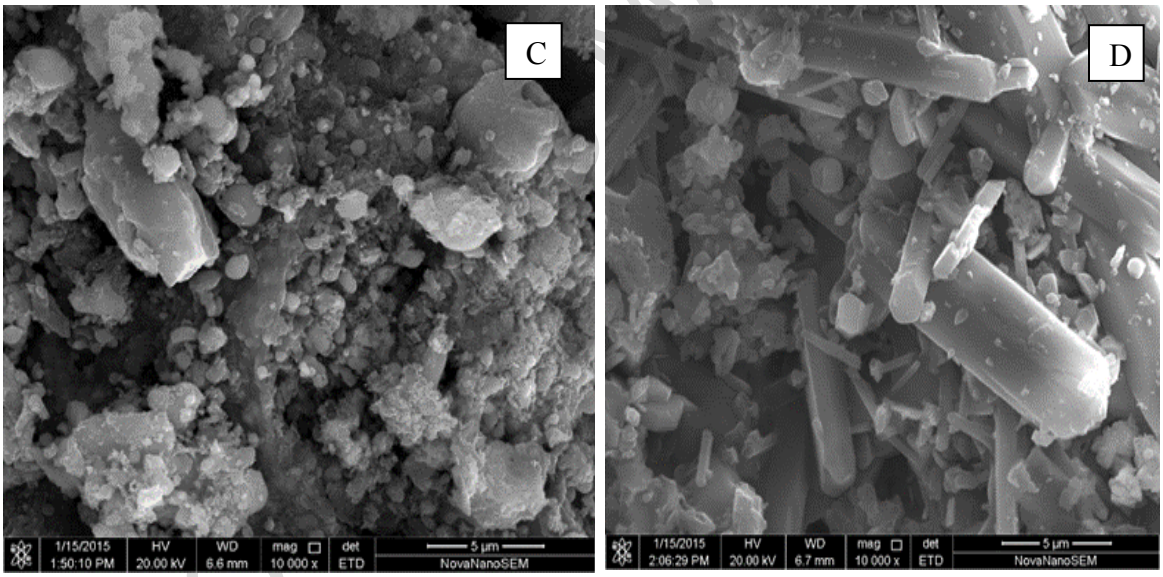


Fig.2.2.Operating situations in the SMT extraction protocol.



(A,B) at 800^{o}C and 900^{o}C for 60 minutes without Cl^- additives.



(C) at 1000^{o}C for 60 minutes without Cl^- additives (D) at 800^{o}C after calcination with 15% Cl^- as KCl and 60 minutes RT.

Fig.3. SEM was used to study the Surface properties of Incinerated Sewage sludge ash before and after calcination with 15%KCl at (800 -1000^{o}C) with RT 60 minutes.

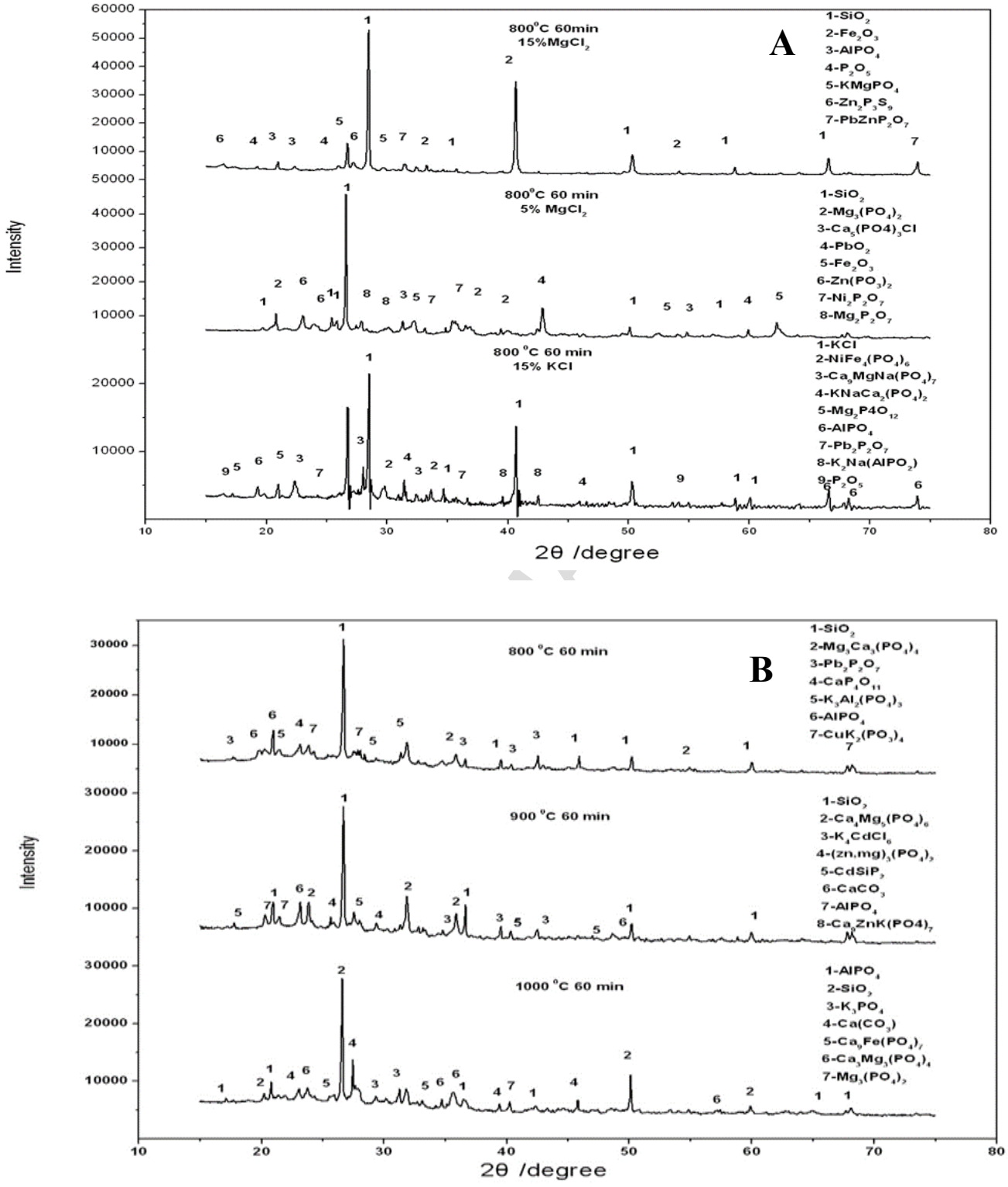


Fig.4. X-ray diffraction model of the sewage sludge ash at (800-1000°C), (A) with Cl^- and (B) without Cl^- additives.

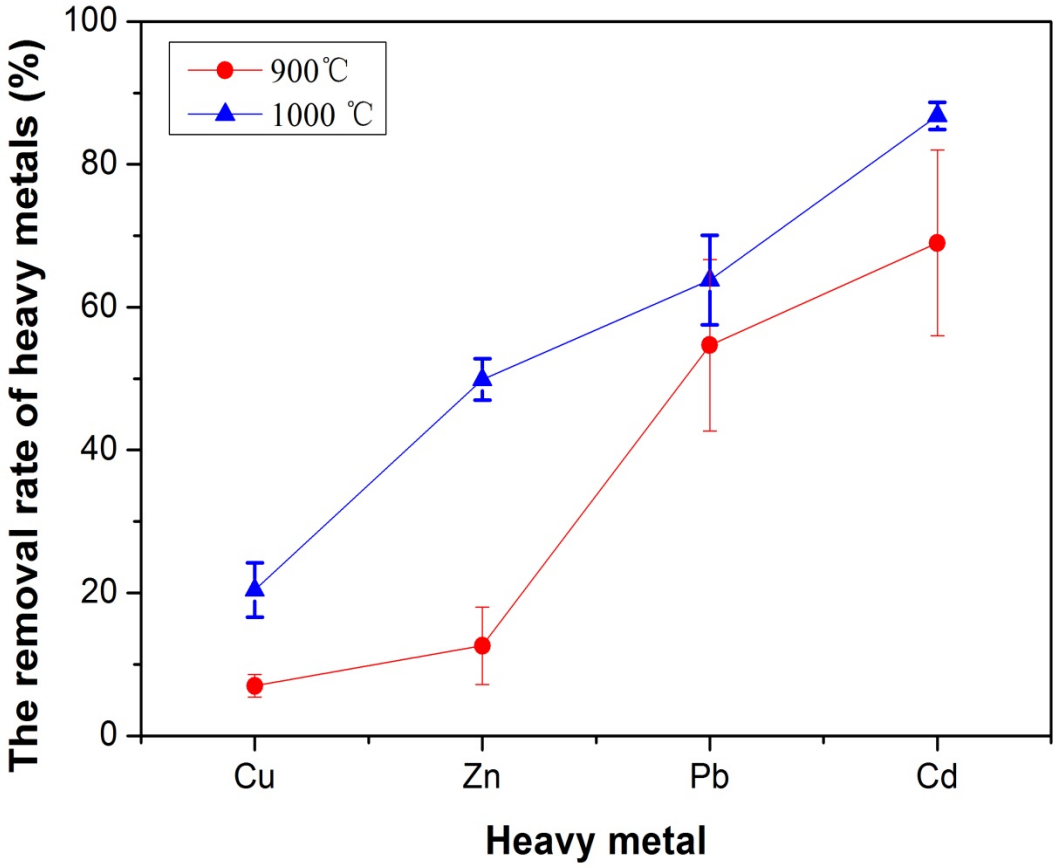


Fig.5.The effects of temperature on heavy metals removal in SSA within 60min retention time.

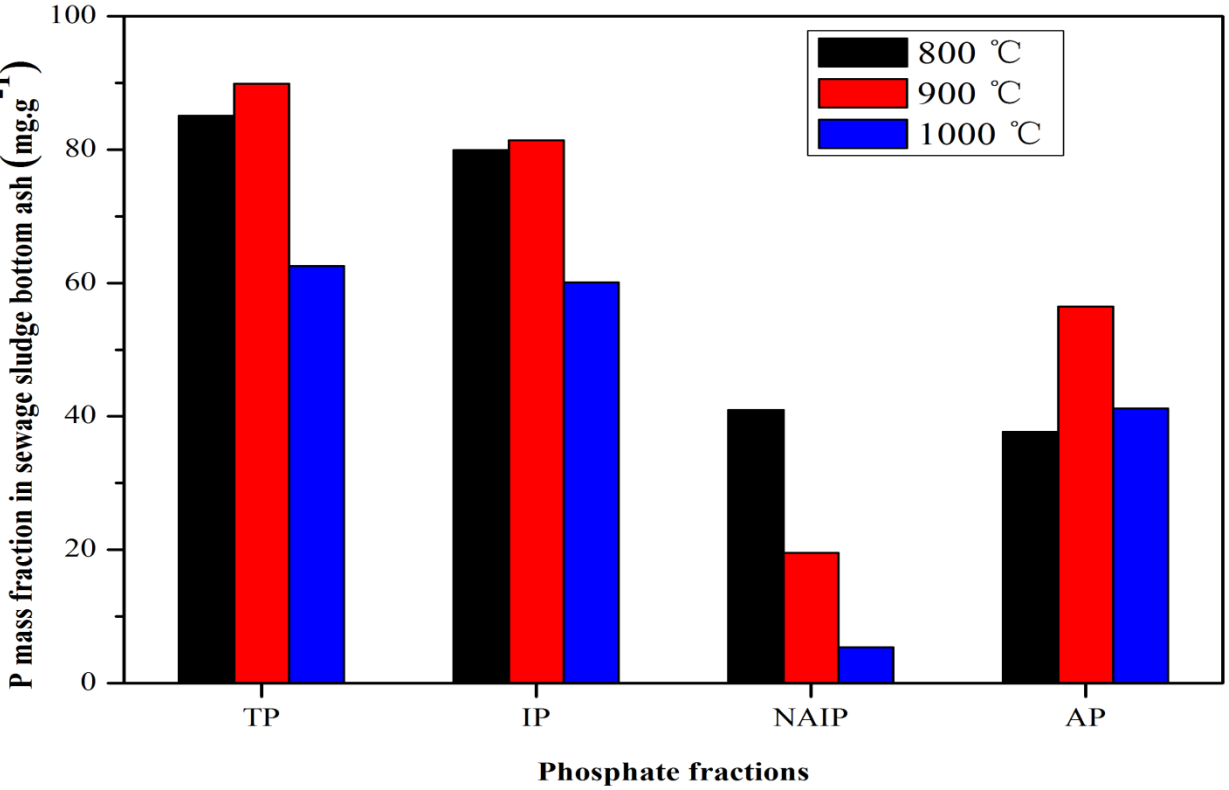


Fig.6. P mass fractions in sewage sludge ash at different temperatures within 60minutes retention time ($mg.g^{-1}$) SSA.

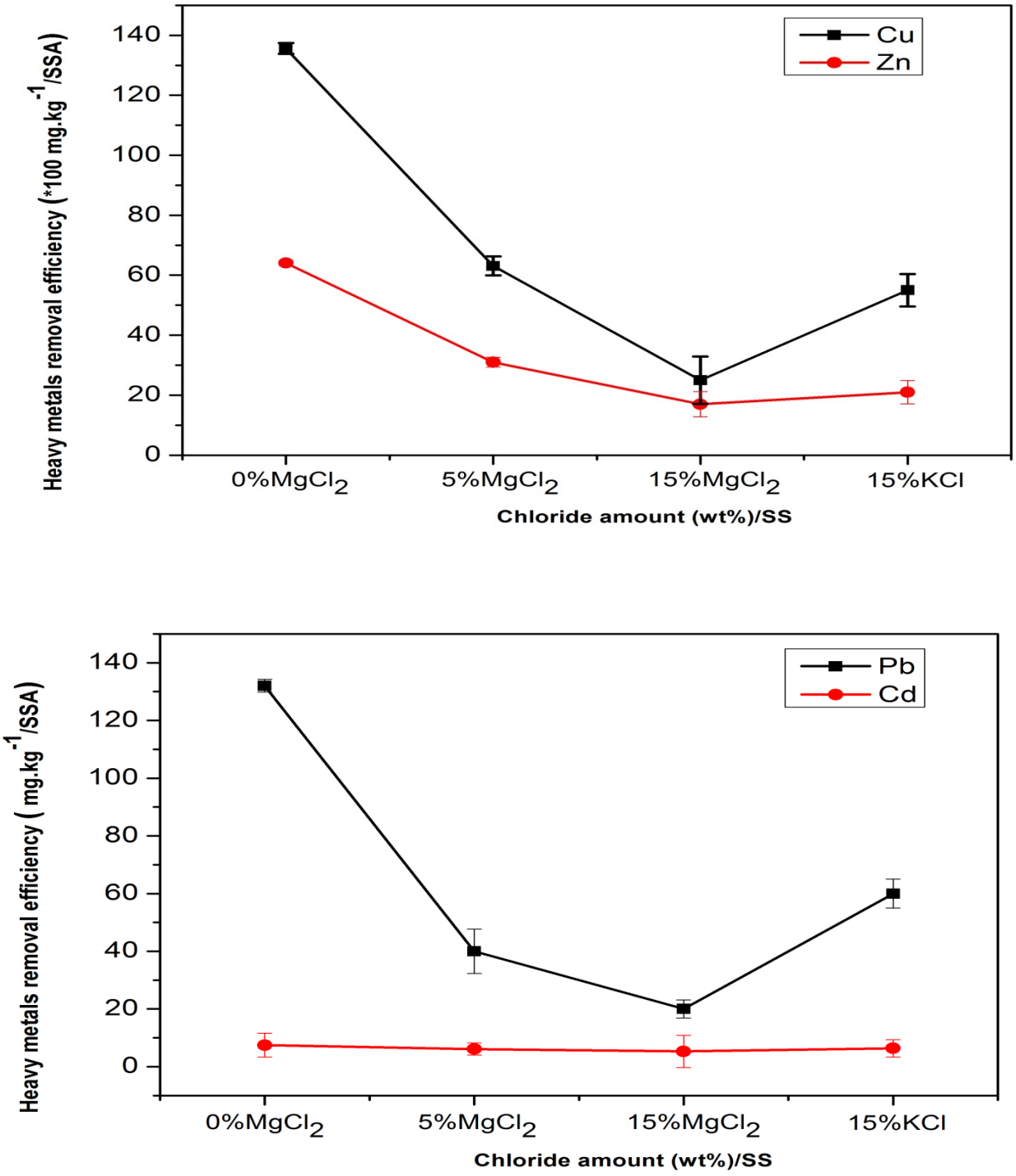


Fig.7. The effects of chlorinating agent on removal efficiency of heavy metals during SSI at 800^{o}C and 60 minutes retention time (mg.kg^{-1}SSA).

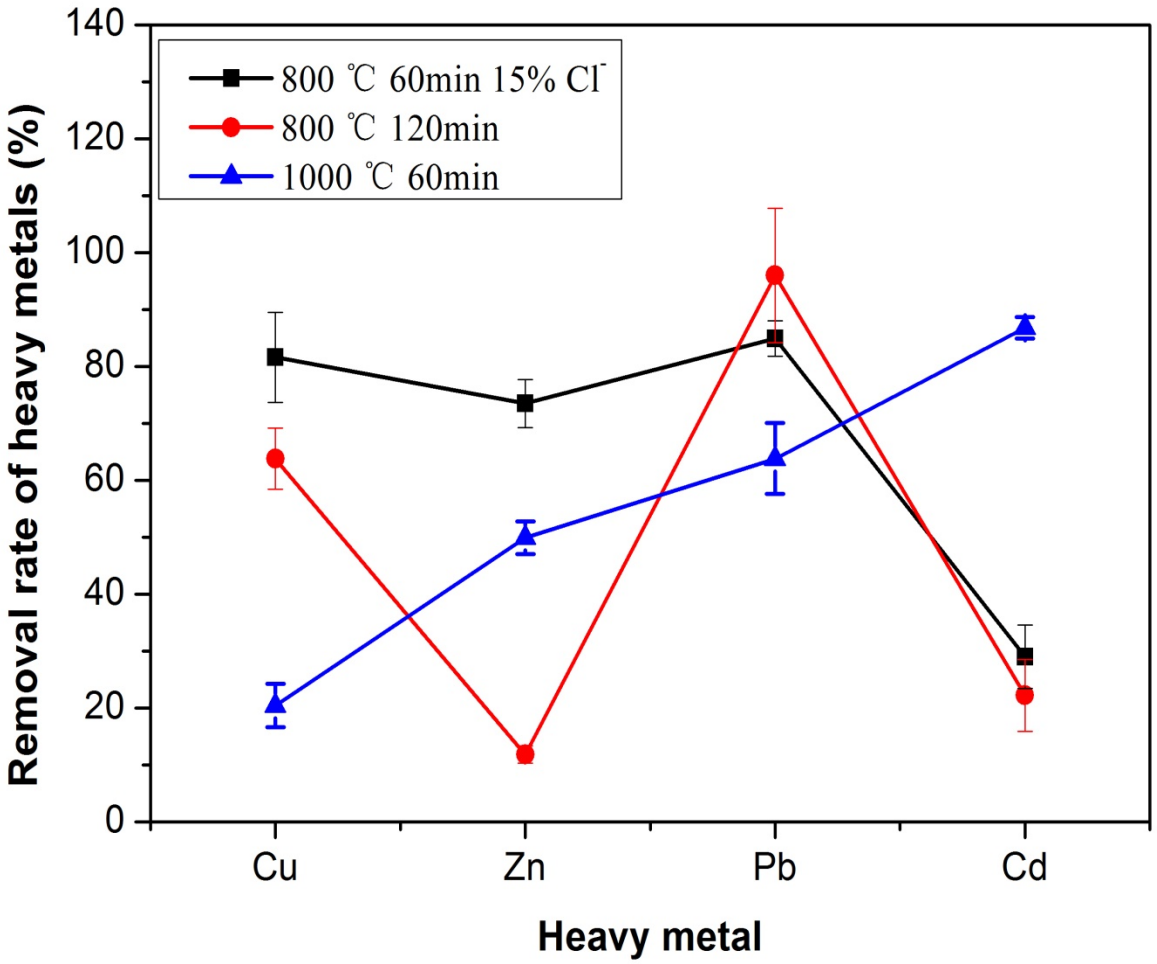


Fig.8. Comparison of the applied parameters on the removal efficiency of heavy metals during sewage sludge incineration (%).

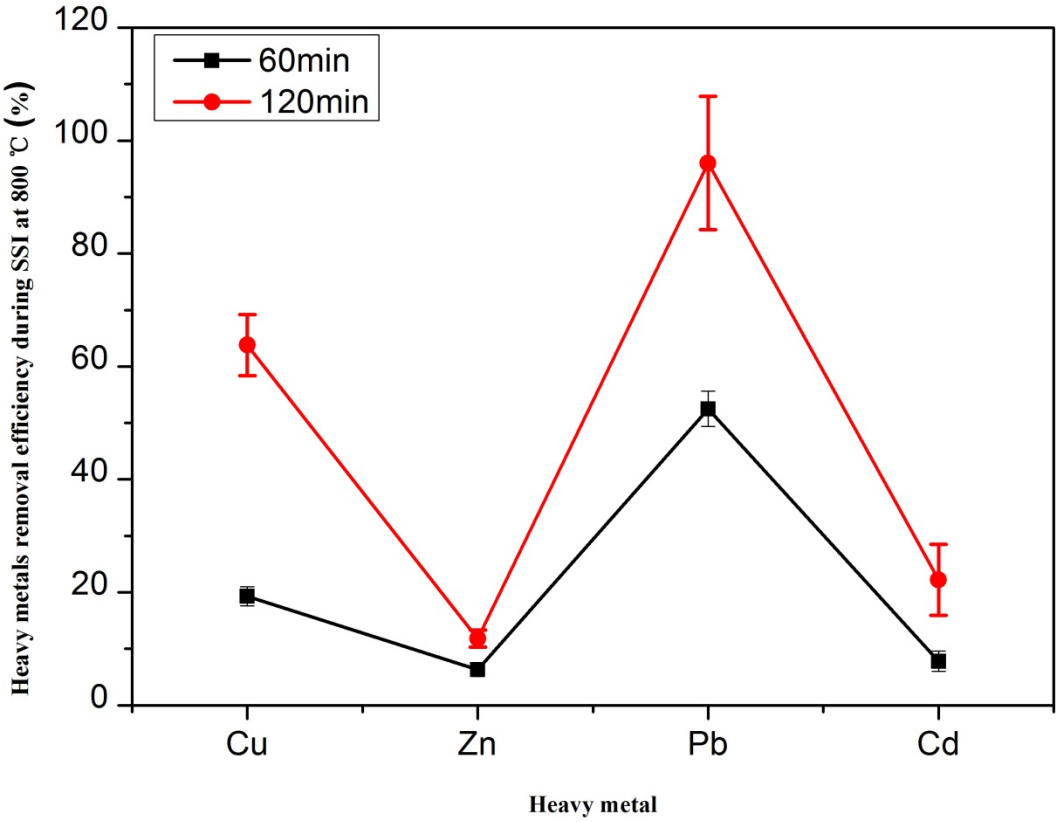


Fig.9. The effects of retention time on heavy metals removal efficiency during SSI at 800°C (%).

Table.1. Immediate and final analysis of dried SS at 105°C (wt%)

Immediate Analysis (wt%, after air-dried)				Final Analysis (wt%, After air-dried)				
M_{ad}	A_{ad}	FC_{ad}	V_{ad}	C_{ad}	H_{ad}	N_{ad}	S_{ad}	O_{ad}
7.12	32.53	8.01	56.2	43.6	8.11	5.9	2.21	40.18

Table.2. Major chemical components of dried SS at 105°C (wt%)

	SiO_2	Fe_2O_3	Al_2O_3	CaO	K_2O	MgO	SO_3	Cl	P_2O_5
(wt%)	24.91	12.32	12.43	15.94	5.2	5.21	6.98	0.31	15.9

Table.3. Phosphorus and heavy metals mass fractions in dried sewage sludge at 105°C ($mg.g^{-1}$)

Element	P	Cu	Zn	Pb	Cd
Mass fraction ($mg.g^{-1}$)	25.29	4.008	1.862	0.08097	0.00448

Table.4. Mass fractions of HM's in sewage sludge ash at temperature between 800 - 1000°C within 60 minutes retention time (mg.kg^{-1}) SSA.

T °C /Elem.	105°C	800°C	900°C	1000°C
Cu	4008.7±51.4	13560±256	12610±209	10800±411
Zn	1862.1±49	6410±60	5600±87	3209±93
Pb	80.97±6.09	132.75±3.09	60±7.5	48±3
Cd	4.479±0.411	7.47±0.310	2.3±0.3	1±0.197

Table.5. Mass fractions of HM's in sewage sludge ash with different amounts of Cl^- additives at 800°C and 60 minutes retention time ($mg.kg^{-1}$) SSA.

additives / Element	5% $MgCl_2$	15% $MgCl_2$	15% KCl
Cu	6310±206	2500±199	5500±301
Zn	3100±51	1700±71	2100±83
Pb	40±3.09	20±6.2	60±3
Cd	6.1±0.121	5.3±0.3	6.4±0.197

Table.6. Heavy metals concentration in SSA at 800^{o}C and different retention time (mg.kg^{-1}) SSA.

R T /Element	30min	60min	120min
Cu	16810±21.4	13560±233	5911±321
Zn	6840±43	6410±56	6033±91
Pb	278±6.29	132±4.12	11±1.3
Cd	8.1±0.52	7.47±0.140	6.3±0.4

Table.7.Mass fractions of phosphorus at different temperature and 60 minutes retention time ($mg.g^{-1}$) SSA.

60min/ P. Fractions	800°C	900°C	1000°C
TP	85.12	89.91	62.57
IP	79.93	81.42	60.1
NAIP	40.95	19.56	5.41
AP	37.7	56.5	41.2