Wet air oxidation (WAO) on sludge treatment and its first industrial application in China

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Abstract: Typical commercial application of WAO on sludge treatment is first used in China, system design and debugging, and effect and cost performance is illustrated in this article. It reduces the temperature and pressure of a typical wet oxidation reaction, and the oxygen supplied is only 30-50% of the COD, which is specifically used to treat sludge. After the treatment, the sludge moisture content from 80% to 45-48%, and become harmless and stabilized, so it can be used as soil for gardens directly or mixed with other materials. As a supplementary carbon source for the nitrogen removal and phosphorus removal process, the separation solution is rich in organic acids and returned to the sewage plant after the heavy metal removal process. The operating cost of the entire process is 180-200 yuan per ton (80% moisture content), mainly for electricity consumption.

1. Introduction
Sludge problem has become a big challenge that needs to be faced and solved during the process of urbanization, especially in China, where there is the highest speed of city formation and development in the world, as well as population. Sewage sludge contains large amounts of water, microorganisms and mineral components[1,2] (Qi and Thapa 2011, Vaxelaire and Cézac 2004), which made sludge treatment and disposal difficult. Some current treatment technologies are listed and regulated by a (draft) Chinese technology policy[3], such as incineration, super-critical oxidation, carbonization, hot drying, lime stabilization and anaerobic digestion (AD),and three disposal and reuse practices as building materials utilization, land use and landfill are taken into account as well[4]. Since no more land can be filled constantly, landfill is not the most recommended technology in China, strict regulations are required in detecting and preventing contamination of soil and ground water. Radical destruction of organic matter and greatest reduction of sludge volume are both achieved by incineration, but potential air pollution and high cost in building and running makes it hard to be wildly applied[5-6]. Anaerobic digestion (AD), which is mostly applied in China (25 sludge treatment plants of 400 waste water plant by the year of 2008)[7] (Wu and et.al 2008) compared with other technology, has been suggested to be most suitable for energy and resource recycle. While high cost in facility construction and low efficiency of gas production raise barriers to its development. Thermal hydrolysis (TH) is a kind of pretreatment usually used before AD, to improve dewaterability of sludge by destroying microbial cells and increase biogas production[8] (Neyens and Baeyens 2003).

In recent years, recover resources from sludge has became the research trend. In the US, over 50
percents of residue after AD is sold out as good fertilizer, which can be divided into class A according to the reducing level of the indicative pathogenic bacteria and nine kinds of heavy metals concentration complies with the Environmental Protection Agency (EPA) requirements. In another hand, recycled sludge as adsorbent, microbial consortium, plant, bulking agent (wheat husk) and nutrients are researched under study of toxic materials in the sludge (Nanekar and et al 2015) as well. The Chinese government believes that the shorter the recycling route, the lower the energy and expense consumption, so that land use of sludge and its treatment methods are under study. Compared to incineration and AD, wet air oxidation (WAO), which is a well-established process for toxic and hazardous organic waste water treatment (Kanhaiya and Anurag 2015), generates minimal air pollution problems, maximum sludge solids reduction and low environmental impacts with a closed-loop water system. The industrial installations of WAO have been put in motion. They operate correctly and often achieve the designed production capacity. But, industrial facilities used in 1990th in the world were closed or reduction in capacity because of high energy consumption with temperature as high as 240-300°C and great pressure of over 10MPa, as well as its serous corrosion by organic acid generated in the process of oxidation. The Athos process by Veolia Water is one of the main WAO sludge treatment technologies currently provided commercially, who operates at temperatures between 250-300 °C, using air or pure oxygen as the oxidant and claimed to produce mineral products, clean gas emissions, and biodegradable liquids. As far as observed, no typical Athos process is employed in China.

In this study, sludge treatment and recycling are combined together in a WAO system, which is modified to produce improved solid for alkaline soil or organic soil base from sludge. The first industrial application of WAO in sludge treatment in China has been researched, from its background, process flow diagram to parameters data during debugging and investment and operation cost, giving out the overall pictures of the project.

2. First industrial application in China Yancang Sludge disposal center

2.1. Background of the project

In recent years, the city of Haining, locating near Hangzhou, has developed very rapidly. Three sewage treatment plants in Haining have been expanded its capacity to 310,000 tons. At present, some of the dehydrated sludge is burned and made into bricks. As the increasing of the amount of sludge and the strict requirement of environmental protection, as well as limitation on land, more effective and land-saving route is needed in this project. WAO is an alternative choice and finally had been chosen to be the technology to treat the sludge produced by sewage treatment plants in Haining. The raw sludge is from waste water treatment plant in industrial zone, which is mixing 70% leather processing waste water and 30% municipal waste water.

At 8th May 2014, the first commercial WAO on sludge treatment plant in China began operating in Yancang (Jiangsu provence of China), treating 100 tons(moisture 80%) sludge everyday. The biggest feature of WAO used in the project is lower reacting temperature and pressure (160-220 °C, 1.5-3.0MPa), with its export solid moisture below 50%, and solid disposal can use as plant soil or matrix to improve soil quantity. Considering its utility, oxidizing 30% of organic which is unstable and perishable is enough.

Sludge treatment workshop located in the waste-water plant, right beside workshop of sludge dewatering as Fig.1, so that dewatered sludge from the plant can be transferred to WAO workshop by screw pump after mixing with polymer dehydrator and going though dehydration centrifuge machines.
In the workshop, tanks and reactors, connected with tubes and control line, are overall controlled by DCS (distributed control system). The key reactor is oxidation reactor on the third floor, which has a volume of 10 m³.

2.2. Illustrate of the process flow diagram
This system mainly consists of three parts as Fig 4.
Mixed sludge and the liquid flowed back, forming slurry with 86-92% moisture, are heated in premix heating part. At oxidation reactor, the oxidation of the organic ingredients starts when temperatures rise between 160 and 180 °C. The oxidized liquor in high temperature is pressed into flash steam tank, which let spare pressure and moisture get out and exchanged in the form of steam. Then sludge about 80°C is piped to the centrifugal dehydration, with the solid product exported out of the system and liquid ones, which is piped back to the premixed part after sedimentation if necessary. Energy and heat recover and exchange sections are designed to lower the energy consumption. Solid product of the line is used as matrix for soil improving or to be land-filled with the moisture below 40%.
Public works and automatic control systems mainly include air compression system, air purification, water recycling system, and energy recovery, as well as three main parts, are controlled by centralized DCS system, with all the data and parameters measured by detectors shown on one screen in control room.

2.3. Parameters during debugging

After construction, adjusting the technology to the raw sludge is important for qualifying the residue to the land use which it planed and promised in the contract, as well as guaranteeing the liquid safe to return to sewage plant as carbon source. As the project was built and run by the professional company, reduce cost on heating is important to limit the cost in running.

During the process of debugging of the system, temperature and reacting time is changeable between a range, and moisture content of residue solid, organic compounds in solid and COD, TP, TN and metal ions in the liquid is important parameter.

Inlet sludge has its parameters as follow table.

| Parameters          | Unit | Value range |
|---------------------|------|-------------|
| Moisture content    | %    | 79-84       |
| Organic content     | %    | 48-65       |
| TP                  | %    | 2.8-3.0     |
| TN                  | %    | 0.8-0.9     |
| Cu²⁺                | mg/kg | 3000-3500  |
| Zn²⁺                | mg/kg | 3000-4000  |
| Ni²⁺                | mg/kg | 300-350    |
| Cr³⁺                | mg/kg | 1000-1250  |
| Cd²⁺                | mg/kg | 0.2-0.33   |
| Pb²⁺                | mg/kg | 100-120    |
| As²⁺                | mg/kg | 49-52      |
2.3.1. Analysis
Moisture content and organic solid content were determined. Each solid sample was dried at 105 ℃, the weight loss represents the moisture, then the residue and container were ignited at 500 ± 5 ℃ and the weight loss recorded as organic. COD, total nitrogen (TN) and total phosphorus (TP) of the solution were analyzed, metal ions in the solid and liquid was estimated by flame atomic absorption spectrometric method after digesting with nitric acid and diluting referring to the Chinese standard series of methods for water quality.

2.3.2. Moisture content of residue solid
The key parameter of the residue solid is moisture content, which determines its volume and weight, furthermore, affects its treat cost. In the system, temperature from 156 ℃ (429K) to 197 ℃ (470K) and reaction time from 5 minutes to 40 minutes were tested on the effect of moisture content, with its result shown in Fig.3.

![Figure 4 Effect of temperature and time on moisture content of the solid](image)

From 429K to 470K, with 30 minutes reacting time, moisture content of residue solid can be much lower than 60%, varied between 44% and 38%. It is certain that during the process of WAO, thermal hydrolysis is also happening, as the sludge is heated to 80 ℃ (353K) in the premixing tank and before going into oxidation reactor, it can under temperature above 120 ℃ as long as 10 minutes when it flows through Electromagnetic heating tube. After thermal hydrolysis, bound water content, particle size and viscoelasticity of municipal sludge decreased, while specific surface area of sludge flock increased [12] (Guohong Feng, et al, 2014). It is accordance with the finding that increased temperature can lead to increasing cake solids after dewatering [13] (Higgins MJ, 2017), but in this system, it suggested that temperature is not the most important parameter to decrease moisture content of residue solid. Reacting time has much more influence on moisture content than temperature does. Compared with 40 minutes’ 38%, 5 minutes reacting time can only get the solid reach 56%, while 15 minutes can get it to 48%. The whole time for WAO is limited in oxidation reactor, while the time for thermal hydrolysis start from 30 minutes before that. No industrial example has been searched about the final moisture content vary with WAO time.

Higher temperature and longer reacting time would be better for the dewatering process. Considering the cost, 170 ℃ (443K) would be enough for the treatment, and the reacting time need to as long as 30 minutes.

2.3.3. Organic compounds in residue solid
Organic compounds is important that can decide how the residue solid perform as matrix of soil improve, and is a parameter which can reflect the oxidation degree of the system. On the other hand, solution COD determined the influence of the discharged solution on the work of waste-water plant. In addition, combined organic content to solution COD, the total oxidation rate and the organic material transferring condition can be shown.
Effect of temperature and time on organic content of the solid and solution COD

With fixed reacting time as 30minutes, as temperature increase, organic material in solid slightly goes up until 453K(180℃),then decreased from 36% to 34% at 470(197℃). Compared with the little effect on solid organic material, reacting time had more efficient influence on organic in solution. Higher temperature gets higher COD in solution, which means organic compounds transferred from solid to liquid at higher temperature. As in the liquid, the organic fraction in solution is total volatile solids (TVs),and can be further divided into volatile dissolved solids (VDS)and volatile suspended solids (VSS)\(^\text{[14]}\) (Foladori et al.,2010). Because of the separate machine the project chose, centrifugal dehydration can not get the two kinds of solids out of liquid, the COD contain them both. During the debugging, the plant added plate frame filter press to separate suspended solids after centrifugal separation.

As organic acids can be produced in the process of oxidation on organic materials, which is a kind of good carbon source of the wastewater plant.

2.3.4. Nitrogen and phosphorus in liquid

Nitrogen and phosphorus in liquid are important in the reuse of the liquid as carbon source to the water plant.

As temperature increase, TP in the solution decrease from 23.3mg/L at 429K(156℃) to 10.9 mg/Lat (170℃) and 6.7mg/L at 453K(180℃).That is the result of the precipitation of phosphate as the Ca\(^2+\),Mg\(^2+\),Fe\(^3+\) and other ions released from the floc and microbiological cells under conditions of high temperature and oxidation. At the same time, TN in the solution has large fluctuation in value and even increase 40% as temperature rising. Protein in cells was broken and decomposed into pieces, and the lighter solid compared to phosphate, the TN transferred from solid to liquid as the it turns to amino acids or even nitrate during oxidation and centrifugal separation.

To measure the TN in the SS form and solution form, the plant use plate frame filter press to separate them after centrifugal separation. The result showed that 70% of the TN was in suspended form, which can be removed by filter. So, the solution after reaction can be reused as carbon source.
after centrifugal separation and plate frame filter press in progress, with its COD varied from 150mg/L to 200mg/L, as well as 0.08mg/L of TP and 9mg/L of TN, which is suitable for water plant.

2.3.5. Metal ions
As it is a water plant in industrial park for leather processing and printing(dyeing), metal ions is important and inevitable factor in the sludge treat process. We checked several kinds of metal ions in the debugging process of the system, such as copper, zinc, chromium, cadmium, nickel, arsenic and lead, both in the solid and liquid phase. When sludge is reacting under 170℃ for at least 30 minutes, the solid and liquid out flow of the system is examined and compared with the Chinese standards separately.

| Metalion | Existence of phase | Unit | Value | Origin sludge value | Standard value | Standard reference |
|----------|--------------------|------|-------|---------------------|----------------|-------------------|
| Cu²⁺     | solid              | mg/kg | 1150  | 3080                | <1500          | Chinese standard[15] |
| Zn²⁺     | solid              | mg/kg | 1620  | 3200                | <4000          |                   |
| Ni²⁺     | solid              | mg/kg | 51    | 329                 | <200           |                   |
| Cr³⁺     | solid              | mg/kg | 333   | 1170                | <1000          |                   |
| Cd²⁺     | solid              | mg/kg | 0.08  | 0.29                | <20            |                   |
| Pb²⁺     | solid              | mg/kg | 51    | 110                 | <1000          |                   |
| As²⁺     | solid              | mg/kg | 36.2  | 50.3                | <75            |                   |
| Cr⁶⁺     | liquid             | mg/L  | <0.01 | <0.01               | <0.5           | Chinese standard[16] |
| Hg²⁺     | liquid             | μg/L  | <0.01 | <0.01               | <0.5           |                   |
| Ni²⁺     | liquid             | mg/L  | <0.02 | <0.02               | <1             |                   |
| Cr³⁺     | liquid             | mg/L  | <0.02 | <0.02               | <1.5           |                   |
| Cd²⁺     | liquid             | mg/L  | <0.008| <0.008              | <0.1           |                   |
| Pb²⁺     | liquid             | mg/L  | <0.04 | <0.04               | <1             |                   |
| As²⁺     | liquid             | mg/L  | <0.01 | <0.01               | <0.5           |                   |

Table 2 illustrates that before the treatment by WAO, the metal ions are most contained in the solid part of the sludge, but after treating, big portion of the metal ions transferred out from the residue solid. It can be inferred that out flow of the process is high in metal ions concentration, to get rid of metal ions and meet the wastewater quality standards for discharge to municipal sewers(CJ 343—2010), the liquid was drained to chemical sedimentation tank with calcium oxide solution, which allow metal ions to settle out in turns of sediments. The liquid value in Table 2 is the concentration of metal ions after sedimentation and ready to go into regulation pool of the wastewater plant, which fully meets the standard and can be supplied to the water plant nearby.

2.4. Investment and operation cost
The total investment of the plant is about 28 million yuan, covering an area of 550 square meters in the water plant near the dehydrating unit. Most of the investment (70%) is spent on the set of equipment installed in the three floor steel plant. 70% of operation cost of this system is considered to be used in heating during temperature rise period. Heat source of the plant is electricity power, which is flexible and plenty in many places. The overall treatment cost is reported to be only 180-200 yuan for one ton of sludge with moisture of 80%. If any steam nearby can be used as heat source, the cost can be further decreased. The residue solid is sold out at a low price to a flower nursery stock base as improved soil which is rich in phosphorus and humus.

3. Conclusion
The article showed the overall picture of the typical commercial application of WAO on sludge treatment and its first use in China, specified in system design and debugging, and effect and cost
performance. Sludge treatment workshop located in the waste-water plant, right beside workshop of sludge dewatering. The system mainly consists of three parts as heated in premix heating part, oxidation reactor, dehydration and recovery section. In the debugging period, the effect of temperature and reacting time on moisture and organic content of the solid, COD of solid and solution, TP and TN in the solution, metal ions in the solid ad liquid. As the result of the precipitation of phosphate and 70% of the TN in suspended form can be removed by filter, the solution is suitable for wastewater plant.

At temperature of 170 °C and time of 30 minutes, the sludge moisture content decreased from 80% to below 40%, and become harmless and stabilized. The liquid flowing through sedimentation tank with calcium oxide solution to settle out metal ions can meet the standard to enter the waste water plant. Organic material in outcome solid vary between 36% to 34% from about 60%. The operating cost of the entire process is 180-200 yuan per ton (80% moisture content), mainly for electricity consumption. The residue solid is sold out at a low price to a flower nursery stock base as improved soil which is rich in phosphorus and humus, while the liquid is drained back to wastewater plant.

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