Study on the Reduction Treatment of ink Sludge in Flexo Printing

Yun Gong*a, Ping Gub, Zhonghua Yuc and Quanhui Tiand
Department of Printing and Packing, Shanghai Publishing and Printing College, Shanghai 200093, China.

*a Corresponding author:331391649@qq.com, b 909084648@qq.com,
c 10559282688@qq.com, d 1034631876@qq.com

Abstract. The paper studied about the characteristics of ink sludge of flexo printing and analyzed the possibility different reduction treatment and disposal. Industrial analysis and elemental analysis to confirm the elemental content, TGA and DTG were used to analyze the weight loss and heat absorption and desorption behavior of dry sludge at different temperature. GC-MS and XRF analysis was applied to analysis the composition and content of the compounds. Three kinds treatment for for ink sludge based on different needs.

Keywords: Reduction Treatment, ink sludge, flexo printing.

1. Introduction
With the increase of environmental protection pressure, the problem of flexo waste has brought great troubles to the enterprises recent years. There is no effective treatment method for flexo-printing waste at home and abroad, almost all the sludge is used to transfer treatment. First, add reagent into the waste liquid to precipitated, then part of the waste water is discharged through the mature water treatment process, and the other part is converted into sludge by adding the coagulant and the flocculant to precipitate the resin, the pigment, the additive and etc. The problem of flexo waste disposal exists in the whole industry of flexo printing, which not only increases the economic burden for enterprises, but also with the increasing environmental protection requirements, the sludge problem brought by the precipitation method is also increasingly prominent and needs to be solved.

2. Physical and Chemical Analysis of Sludge
The experimental ink sludge was Shanghai Jielong Printing Factory and Shanghai Xinhua Printing Factory. The appearance is black and the water content is about 80%. The industrial analysis and elemental analysis results are shown in Table 1. Industrial analysis is based on the industrial analysis method of coal (GB/T 212-2008), the contents of C, H, O, N and S were determined by elemental analyzer (VARIO EL cube, Germany), and the O content was calculated by subtraction [1].
Table.1 Industrial analysis and elemental analysis of ink sludge

| Industrial analysis (%) | Elemental analysis (%) |
|-------------------------|------------------------|
| M<sub>ar</sub>         | 78.84                  | H          | 1.17       |
| M<sub>d</sub>          | 1.02                   | C          | 40.78      |
| V<sub>d</sub>          | 60.43                  | N          | 5.26       |
| A<sub>d</sub>          | 33.33                  | S          | 0.59       |
| FC<sub>d</sub>         | 5.22                   | O*         | 19.46      |
|                        |                        | HHV/MJ·kg⁻¹ | 117.57     |

ar: as received basis, d: dry basis O*: subtraction method: O=100-C-H-N-Ash
HHV=(3.55 C²-232C-2230H+51.2C×H+131N+20600)×10⁻³

TGA (Diamond TGA/DTA, PerkinElmer Instruments) were used to analyze the weight loss and heat absorption and desorption behavior of dry sludge at different temperature. Figure.1 shows the TG and DTG curves of dry ink sludge at a heating rate of 20°C/min under a nitrogen atmosphere.

Figure.1 is the TG and DTG curve of dry ink sludge at 20°C/min heating rate under the nitrogen atmosphere. It can be seen that the pyrolysis of ink sludge can be divided into three stages, the first stage is the drying stage, which occurs at about 40 to 160°C, and the weight loss is about 2% at this stage. The second stage is the volatilization analysis stage, which occurs at about 160-550°C, the reaction is most active at this stage, and the weight loss is about 58%. The rate of weight loss is the fastest at 445 °C and reaches 9.5%. The third stage is the stage of continuous decomposition of residual organic compounds and the decomposition of minerals, which occurs at about 550–950°C, weight loss is around 8%, and weight loss is less at high temperature. According to the results of Figure.1, pyrolysis experiments of dry sludge were carried out at 500, 600, 700, 800 and 900°C, and the corresponding pyrolysis residues were named PR500, PR600, PR700, PR800, and PR900.

![TGA and DTG curve of ink sludge at 20 °C/min heating rate](image)

The pyrolysis experiment research of ink sludge are carried out under the above five temperatures. Under different temperatures, the yield of gas-liquid-solid three-phase material and its distribution condition are shown in Figure.3. It can be seen from the figure that as the reaction temperature rises, the gas yield increases, and the solid residue yield is opposite, while the tar yield increases first and then decreases. When the temperature rises from 500°C to 900°C, the gas yield is significantly increased.
from 21.7% to 44.3%; while the solid residue yield is reduced from 48.5% to 37.4%; when the temperature rises from 500 °C to 600° C, the tar yield is increased from 29.8% to 30.5%, the yield decreases to 18.6% as the temperature rise further to 900°C. The above results show that the change of ink sludge material yield with temperature in pyrolysis process is consistent with other researchers' reports on similar waste pyrolysis [2]. The above research results show that after the wet sludge was dried, the sludge volume was reduced to 21.3%, and the volume reduction rate reached 78.7%; after the dry sludge was pyrolyzed, the coke volume reduction reached about 55%. It was converted into wet sludge, namely the volume reduction rate of wet sludge was about 90% after drying and pyrolysis. From this aspect, pyrolysis technology is an effective means of quantitative reduction disposal of ink sludge.

The water was removed from pyrolysis liquid recovered at different temperatures with anhydrous cupric sulfate, 0.45μm nylon filter membrane was used to filter, and the tar component was analyzed with GC-MS. The analysis results of GC-MS are shown in Table.2. As shown in Table.2, the tar pyrolyzed by ink sludge is a very complicated mixture, which mainly contains chain hydrocarbon, benzene series, polycyclic aromatic hydrocarbon and various organic compounds.

| Peak Number | Retention Time | Chemical Name | Chemical Formula | Area % 500°C | 700°C | 900°C |
|-------------|----------------|---------------|-----------------|--------------|--------|--------|
| 1           | 2.8198         | Toluene       | C7H8            | 11.48        | 20.66  | -      |
| 2           | 2.9914         | Hexane, 2-methyl-4-methylene- | C8H16 | 5.00 | - | - |
| 3           | 4.0192         | Benzene, 1,3-dimethyl- | C8H10 | 13.95 | - | - |
| 4           | 4.5262         | Styrene       | C8H8            | 40.70        | 30.40  | -      |
| 5           | 5.1447         | Benzene, (1-methylethyl)- | C9H12 | 3.26 | - | - |
| 6           | 6.3878         | alpha-Methylstyrene | C9H9Cl | 16.28 | 3.64 | - |
| 7           | 7.4614         | 1-Hexanol, 2-ethyl- | C11H24O | 3.29 | - | - |
| 8           | 7.8773         | Indene        | C9H8            | -            | 4.21   | -      |
| 9           | 11.5856        | Naphthalene   | C10H8           | -            | 15.13  | 25.74  |
| 10          | 14.5301        | Naphthalene, 1-methyl- | C11H10 | -  | 3.77 | 4.05 |
| 11          | 16.7423        | Biphenyl      | C12H10          | -            | 3.63   | 16.87  |
| 12          | 18.505         | Biphenylene   | C12H8           | -            | -      | 15.01  |
| 13          | 21.7141        | Fluorene      | C13H10          | -            | -      | 6.28   |
| 14          | 23.3145        | Benzene, 1,1’-(1,3-propanediyl)bis- | C15H16 | - | 3.41 | - |

It can be seen from Table.2 that the composition and content of the compounds in the tar have significant changes at different temperatures. When temperature is 500°C, the tar is mainly styrene (40.70%, area percentage), benzene series (toluene, xylene) (25.43%) and 1H-Indene (16.28%). When temperature is 700°C, the tar mainly contains styrene (30.40%), toluene (20.66%) and naphthalene (18.90%). When temperature is 900°C, the composition of tar mainly contains naphthalene (25.74%), biphenyl (16.87%) and biphenylene (15.01%). When the reaction temperature is 500-700°C, the content of benzene series and derivatives all exceed 50%. From the nature of the pyrolysis material, the components can be relatively easily separated; higher value chemicals can be obtained after separation, such as styrene.
The results of elemental analysis of dry sludge and pyrolysis residues at different temperatures are shown in Figure 2. The carbon content of the dry ink sludge is 40.78 wt%, and the contents of nitrogen and sulfur are 1.17 wt% and 0.59 wt%, respectively. It shows that the carbon content in the ink sludge is higher, and the contents of nitrogen and sulfur are lower, which is close to the contents of nitrogen and sulfur in most coal mines of our country [3, 4].

XRF analysis was conducted on ink sludge and pyrolysis residue. As shown in Table 3, the main metal elements in the raw sludge and pyrolysis residue are Al, Ca, Fe, Ti, Cu, V, Mn, Zn, etc., and the non-metal elements are mainly Si, S, Cl, P and so on. Among them, Al is the highest content of ink sludge, probably because a large amount of Poly aluminum Chloride is added when treating waste water. Secondly, the higher content of elements is calcium and silicon. The contents of Al, Ca and Si element in the pyrolysis residue rise with the increase of pyrolysis temperature, it shows that these elements mainly exist in the form of inorganic substances and a small amount escape to liquid phase and gas phase. The temperature does not change much for the rest of the metal elements; it shows that most of the metal is left in the pyrolysis residue.

**Table 3** XRF analysis of ink sludge and pyrolysis residue (wt%)

| Element | raw sludge | SC500  | SC600  | SC700  | SC800  | SC900  |
|---------|------------|--------|--------|--------|--------|--------|
| Al      | 33.24      | 32.97  | 34.32  | 36.3   | 31.3   | 25.96  |
| Ca      | 20.18      | 24.64  | 26.04  | 27.11  | 35.43  | 39.11  |
| Si      | 18.1       | 19.13  | 15.63  | 14.41  | 14.72  | 16.02  |
| Fe      | 10.77      | 7.97   | 8.82   | 9.93   | 7.47   | 8.23   |
| S       | 4.99       | 4.38   | 3.95   | 2.38   | 2.93   | 4.01   |
| Cl      | 4.01       | 2.67   | 2.37   | 1.95   | 2.03   | 2.37   |
| Ti      | 3.98       | 2.53   | 2.67   | 3.13   | 2.87   | 2.73   |
| P       | 2.94       | 4.95   | 4.86   | 3.3    | 2.38   | 0.35   |
| Cu      | 0.58       | 0.34   | 0.49   | 0.58   | 0.28   | 0.34   |
| V       | 0.54       | 0.23   | 0.35   | 0.39   | 0.25   | 0.45   |
| Mn      | 0.48       | 0.03   | 0.17   | 0.09   | 0.13   | 0.15   |
| Zn      | 0.19       | 0.17   | 0.33   | 0.43   | 0.21   | 0.27   |
3. Treatment Plan of Sludge Reduction

The physicochemical analysis result of sludge, ink sludge has a high burning value, and pyrolysis technology is low-cost effective way to reduce; no harm, stabilize and recycle ink sludge. The flow diagram of ink sludge pyrolysis was designed, and the energy balance of sludge pyrolysis was calculated, it was found that the energy requirement of sludge drying and pyrolysis with 65% water content did not need external supply. However, the implementing premise of this plan is that the amount of sludge is relatively large, the pyrolysis machine needs a lot of energy to start up in actual production, if the amount of sludge is not enough, the pyrolysis oil produced is not enough, and it is enough to offset the startup energy consumption. Therefore, it is suitable for enterprises with a large amount of sludge. At present, most of the flexographic printing enterprises are small and medium-sized enterprises, which cannot reach 1 ton sludge amount per day. Therefore, the solutions for ink sludge are mainly the following three kinds [5].

First, the characteristic of high heat value of ink sludge is used to conduct resource treatment, this kind of plan needs a large amount of sludge, and the sludge needs to be uniformly recovered and then concentrated and pyrolyzed. At present, printing enterprises are relatively scattered, there is no centralized park, and the future printing industry parks can adopt this centralized resource handling method.

Secondly, in allusion to the relatively scattered state of the current flexographic printing enterprises, there is no company intensively recovers sludge, can only be solved by the enterprise itself, and the drying and semi-drying reduction treatment is a compromise treatment. Sludge drying and semi-drying in other industries, such as municipal sludge, power plant sludge, chemical sludge, etc., have relatively mature treatment for reference. At present, the solution to sludge drying/semi-drying is that the sludge undergoes preliminary dewatering and deep dewatering, and finally reaches 40-50% moisture content. The preliminary dewatering is mainly carried out by centrifuge, screw sludge dewatering machine, filter press, etc., and then enter into deep dewatering, which can be added to the molding process, mainly increase the surface area of the sludge, save dewatering time and energy consumption, and deep dewatering mainly uses dryers, there are many kinds of dryers at present, different principles and energy consumption, and can be selected according to the output of sludge.

Third, the waste ink is retrieved and as black ink, this method saves costs and recycles, and meets the current environmental protection theme. This research is in the experimental stage, recovered flexographic sludge after sedimentation, separation and regeneration, recycled ink is obtained, whose various indicators are basically similar to standard sample ink index, at present, the printed products have been tested by SGS, and the printing quality is indistinguishable to the naked eye, waste ink recovery needs to establish supporting management and standard, and expects it to be recognized by the government and the market like recycled paper in the future.

Fourth, the reduction of sludge source is also a method of sludge reduction. In the source of wastewater treatment, the ink wastewater is pretreated by adding some adsorption and catalytic materials, thereby reducing the amount of reagents in the later stage. This method is in the enterprise research stage.

4. Conclusion

Many enterprises are nagged by problem of ink waste, and various enterprises are now exploring solutions based on their needs. The solution of this problem requires coalition and benefit by mutual discussion of colleges, enterprises and industry, and jointly explores several standard solutions for ink sludge to promote, brings benefit to industry and promotes green printing.

Acknowledgements

This study is sported by Lab of Green Platemaking and Standardization for Flexographic Printing.

References

[1] Friedl A, Padouvas E, Rotter H, et al. Prediction of Heating Values of Biomass Fuel from Elemental Composition[J]. Analytica Chimica Acta, 2005, 544(1–2): 191-198.
[2] Menéndez J A, Inguanzo M, Pis J J. Microwave-induced Pyrolysis of Sewage Sludge[J]. Water Research, 2002, 36(13): 3261-4.

[3] Wu Daishe, Zheng Baoshan, Tang Xiuyi et al. Contents and Distribution of Nitrogen in Chinese Coals[J]. Earth and Environment, 2006, 34(1):1-6.

[4] Hu Jun, Zheng Baoshan, Wang Mingshi et al. Distribution and Forming Cause of Sulfur in Chinese Coals[J]. Coal Conversion, 2005, 28(4):1-6.

[5] Gu ping, Gong yun et al. Study on the reduction treatment of flexo sludge[J]. Printing Field, 2018.12.10-12.