Model for Optimizing Sustainable Reuse of Shale Gas Waste Water by Pre-oxidation with Membrane Separation Technique

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Abstract. The purpose of this study is to establish a model to analyze and compare different types of pre-oxidation technologies in shale gas backflow, so as to guide actual production. With the progress of membrane-based processes, membrane separation technique shows great potential in shale gas flowback and produced water (SGFPW) reuse. But membrane fouling due to high concentration of organic matter is still a big problem. Therefore, using integrated process, which combines pre-oxidation with membrane separation, is a good way to deal with membrane fouling. However, there are various kinds of oxidation technologies that can be used into shale gas wastewater treatment, meaning that there needs to be a scheme to guide which technology can do best in different situations. In this paper, the output-output model is used to analyze the pre-oxidation technology. The current pre-oxidation technology is divided into two types, among which the most representative ozonation and Fenton oxidation are selected as examples, and the capital investment in this link is taken as the index for analysis. It is concluded that Fenton oxidation method can be used when the amount of waste water is small, but when the amount of waste water is large, the economic benefit of ozonation is higher. Similarly, this model can be widely applied to the analysis and comparison of a large number of pre-oxidation technologies in shale gas wastewater, and can also be modified as the technology advances.

1 Introduction

Shale gas, as a new type of energy that is increasingly becoming an important part of fossil energy due to its high storage capacity, leads to the exploitation of shale gas in many countries around the world [1]. For example, shale gas in South Sichuan Shale gas base have reached to 2011 trillion cubic meters, which can meet a large part of China's fossil energy market demand. Similarly, shale gas could complement world energy market.

However, shale gas flowback and produced water(SGFPW) is one of the environment consequences caused by shale gas exploitation. Because hydraulic fracturing is widely used in recovering shale gas, and the fracturing fluid is mixed with variety kinds of chemical additives [2]. It can also lead to the high concentration of organic matter, which contains a lot of toxic organic matter.

In order to avoid the wastewater pollution to the environment and to recycle the water resources, membrane technologies is a potential way for sustainable reuse of shale gas wastewater. However, high concentration of organic matter in the flowback water is an important factor for membrane fouling and degradation [3], so it is necessary to carry out pre-oxidation before membrane treatment to reduce the concentration of organic matter. But there are variety kinds of pre-oxidation technologies, and each of them has its strengths and weakness. This paper will carry out modelling analysis on pre-oxidation technologies at present, which can guide the selection on pre-oxidation under different circumstances.

2 Type of pre-oxidation technologies

At present, there are many oxidation technologies used in industrial wastewater purification. What is more, as distributed in different places, the shale gas explorations are different (such as water resources, distance to the sewage treatment plant), and lead to the most suitable technologies for shale gas are different. From the perspective of input/output models, it can be divided into two categories. One of them is represented by ozone-oxidation, which has a large initial investment but a low capital requirement for continuous work. The other type does not require a large early investment, but the cost of continuous work is higher than the former type, which can be represented by Fenton oxidation.

3 Model for comparing the pre-oxidation technologies

Input/output model can be used to the represent relationship between production of goods and exchange

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of materials between economic sectors within a region [4]. It can also analyze the inputs and outputs at a given stage of industrial production to guide decision makers in choosing different options. Modeling analysis of pre-oxidation using input-output model can be calculated by the following equation:

$$TK=Kin - Kout. \quad (1)$$

Where TK is total capital of this oxidation, Kin is invested capital and Kout is produced capital. The Kin and Kout can be evaluated by equation (2) and (3):

$$Kin= Ceq+Ce+Ctr \quad (2)$$

$$Kout=Pm+Pe \quad (3)$$

Where Ceq is the cost of reaction equipment and the Ce and Ctr are the cost of energy and transportation. In equation (3), Pm is price of water and other chemicals saved after treatment and Pe is the price of energy saved energy. The average expenditure (AE) can be figured out by TK and the volume of treated sewage.

$$AE=TK/V. \quad (4)$$

Because Pm and Pe are changeable according to the different treatment conditions and the output generated by this step is much smaller than the input based on the current research and practical application, the Kout will be omitted in the modelling in this paper. However, equation(3) is also necessary because many pre-oxidation technologies can play the role of resource enrichment. For example, the pre-oxidation of ferrates can enrich some resources like nitrogen, which will be enriched into the form of sludge because of iron colloids converted from the ferrates. This kind of sludge can be used as fertilizer, which will be a part of Kout. This step also has the potential to generate revenue, and if this step generates revenue, equation(3) need to be considered.

3.1 Ozone-oxidation

Ozone-oxidation, which can be called pre-ozonation when it acts as a pre-oxidation step, is a technology that uses oxygen molecules to obtain energy by electron excitation generated by high density current on the anode surface of the reactor, then polymerizes them into ozone molecules, and uses the oxidation property of ozone to oxidize organic matters in water. This kind of oxidation has the advantages of green, high efficiency and no secondary pollution [5], which means it is well suited as a method of pre-oxidation.

The input and output average capital are as follows; the capital of electric energy refers to the cost of treating each ton of shale gas wastewater.

Table 1. The most important capital type of ozone pre-oxi dation [6].

Ozone generator and transportation fee	100000	¥
Electric energy	154.2857	¥/ton

Using the obtained data and the above equation, the total input and average input per ton of wastewater required for an ozone generator to treat 100 ton of wastewater are plotted (figure1).

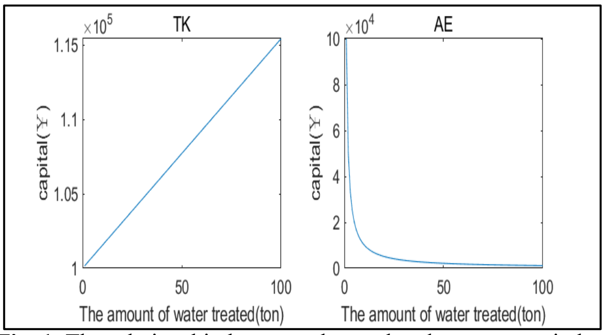

Fig. 1. The relationship between the total and average capital of an ozone generator for treatment of shale gas wastewater and the amount of water treated

It can be seen from figure 1 that the initial investment of pre-ozonation is relatively high, but with the increase of the weight of treated water, the price per unit of wastewater treatment will drop rapidly at the first 20 ton of water and then approaching the consumption of electric energy.

3.2 Fenton-oxidation

Fenton-oxidation is a very effective method for the treatment of organic wastewater, which has the advantages such as good oxidation effect and simple operation. The Fenton reagent is composed of ferrous salts(Fe2+) and hydrogen peroxide, and it uses ferrous ions to react with high concentration hydrogen peroxide based on the reaction principle [7].

As a still developing technology, Fenton has great potential and feasibility in the pre-treatment of shale gas wastewater. The input and output average capital are as follows:

Table 2. The most important capital type of Fenton-oxidation [6].

Fenton reactor	12000	¥
Fenton raw material	14999	¥/ton

The quality of Fenton regent required to treat each ton of wastewater can be calculated, which is 218g/ton [8]. So the capital of Fenton material for treating each ton of shale gas wastewater is 3269.78 ¥.

Using the obtained data and the above equation, the total input and average input per ton of wastewater required for an Fenton reactor to treat 100 ton of wastewater are plotted(figure 2).

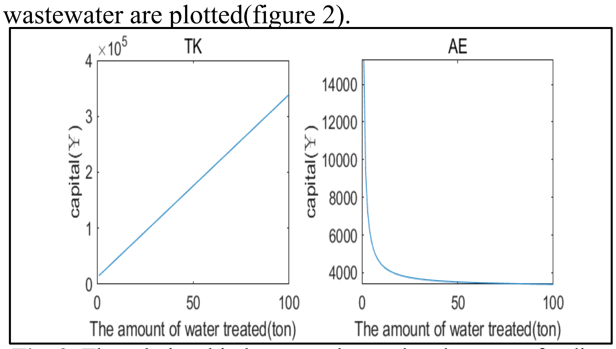

Fig. 2. The relationship between the total and average funding of a Fenton reactor for shale gas wastewater treatment and the amount of water treated

As can be seen from figure 2, the initial expenditure is low, but as the quality of wastewater treatment increase, the expenditure per ton of wastewater treatment approaches the cost of Fenton regent.

3.3 Comparison

Using model to compare the expenditure of these two methods, figure 3 can be obtained.

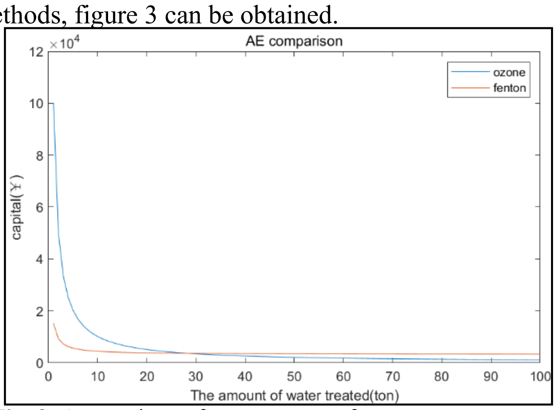

Fig. 3. Comparison of average cost of wastewater treatment between an ozone generator and a Fenton reactor

It can be seen from figure 3 that the AE of ozonation at the initial stage of application is much higher than the of Fenton oxidation. However, with the improvement of water quality, the AE of ozonation rapidly drops and soon fails below the AE of Fenton oxidation.

Therefore, in practical engineering, this model can be used. For example, when the average amount of wastewater in each ozone generator or Fenton reactor is small, Fenton oxidation can be used, otherwise, if this value is high, preozonation is a better choice.

4 Discussion

In this paper, the input/output model is used to solve the selection of preoxidation scheme for shale gas wastewater. The equation is relatively comprehensive, but in the model built in this paper, lots of technologies have not been applied in actual production, so the link gains some relatively small amounts. When people start modeling, this part of value is chosen to be ignored. But if the technology for energy and matter collection improves in the future, there will be benefits. Then the required model can be obtained simply by putting this value into the equation when modelling.

The capital required by the pre-oxidation link is taken as the standard in this paper. The mature ozonation technology and Fenton oxidation technology in wastewater pre-treatment were analyzed in order to compare the two in the demand of different wastewater treatment capacity, and a more suitable scheme can be selected quickly and convincingly. According to the model in this paper, when the amount of water needed to be treated is little, oxidation techniques, such as Fenton method, are more appropriate. However, when the amount of wastewater is large, ozone oxidation is more economical than Fenton oxidation. Similarly, other techniques, such as ferrate oxidation and persulfate oxidation, can also be modeled and compared in this way, after they can be applied to actual shale gas wastewater treatment. In addition, if other criteria such as environmental life cycle assessment (LCA), water footprint and carbon footprint need to be considered. This model can also be used for analysis as it has great potential in the pre-oxidation stage of shale gas. It is instructive for the sustainable reuse of shale gas backflow, and has certain theoretical significance and application value.

5 Conclusion

As an increasingly important energy source in the fossil energy market, shale gas is constantly being exploited. So the harm of SGFPW to the environment also needs to be paid attention to. However, membrane technology has many shortcomings in treating shale gas wastewater separately, most of which are caused by high concentration of organic matter in wastewater. Therefore, the combination of pre-oxidation technology and membrane separation technology has great potential. There are many kinds of preoxidation technologies, among which there are two ways. The initial investment is quite large, but the subsequent investment is small, which can be represented by ozone oxidation. The initial investment is smaller, but subsequent investment is larger than the former, represented by Fenton oxidation. Therefore, how to choose the proper preoxidation technology is very in practical engineering.

The input-output model in this paper can solve this problem well. By calculating the capital investment of the pre-oxidation step, this model compares two oxidation technologies which are mature at present, and plays a guiding role in the selection of technologies under different circumstances. For instance, Fenton is used for pre-oxidation when the amount of treated wastewater is small, and ozone is used for pre-oxidation when the amount of treated wastewater is large And when the input or output changes, this model also has strong adaptability. However, the model also has its shortcomings. For example, different pre-oxidation technologies have certain differences in the treatment degree of shale gas wastewater, which will lead to the subsequent film degradation rate, making the whole wastewater treatment process cost different than expected. Therefore, in the future, subsequent membrane separation steps will be added on the basis of this step, which can greatly improve the stability of the model and provide more effective guidance for the actual production.

Acknowledgments

The author is grateful to Jane, Allison, prof. Aidong Yang and Xuanwei Qi. Without their help, this paper cannot be completed.

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