

THE SELF-DESULPHURATING CHARACTERISTICS OF HIGH  
SULPHUR OIL SHALE IN FLUIDIZED BED COMBUSTOR

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ABSTRACT

Experiments on high sulphur oil shale with 1.42–1.49% sulphur and a net heating value of 4857 kJ/kg (or 1160 kcal/kg) whose ash contained 27.72% CaO and 1.28% MgO were performed in a laboratory-scale fluidized bed combustor. The effects of bed temperature, bed pressure drop (or bed height), excess air coefficient and particle diameter on sulphur retention were investigated during the experiments. It is found from the experiments that the oil shale has great capability of self-desulphurating without additional limestone or other sorbents, because of its ash with high CaO content. By changing the operating parameters, the sulphur capture efficiency is in the range of 86% to 99%. The concentration of SO<sub>2</sub> in flue gas varies from 200 ppm to 400 ppm. Among the operating parameters, the bed temperature has the most significant effect on sulphur retention, and the optimal bed temperature is 850 °C.

1. INTRODUCTION

Oil shale mines have been found in many regions of the world and the workable reserves of oil shale are great. There are two ways to utilize oil shale. One is to extract shale oil from it and the other is to use it as fuel. China has abstracted oil from oil shale for about half a century and a lot of successful experiences have been obtained. On the other hand, China has also used low sulphur oil shale as fuel in industrial boilers for more than a decade. In recent years, fluidized bed boilers in small-scale power plants near mines come to use oil shale as fuel, but using high sulphur oil shale as fuel still remains totally new for us. In order to supply some information to the utilization of high sulphur oil shale as power plant fuel, the experiment with high sulphur oil shale were conducted. The oil shale tested in the experiment contains 1.42–1.49% sulphur and has a net caloric value of 4857 kJ/kg (or 1160 kcal/kg) Its ash contains 27.72% CaO and 1.28 MgO

2. EXPERIMENTAL EQUIPMENT AND CONDITION

The experimental equipment is shown in figure 1 and consisted of a

tube fluidized bed combustor heated by electricity, a screw feeder, a forced-draft fan, an induced-draft fan and a gas analyzer. The inside liner of the combustor was silicon-carbide tube of 100 mm in diameter and a length of heating wire twined round the tube. A thermometric instrument and an isothermal temperature regulator were employed to measure and control the bed temperature. There were nine nozzles on the air distributor. The aperture ratio was 1.44%. Air was used as fluidizing gas. The feeder above the combustor put the crushed oil shale into the combustor continuously. The feed rate was 1–2kg/h. The combustor was kept in a little positive pressure. The combustion products went through a filter and a moisture eliminator, then were delivered into the gas analyzer by vacuum pump. The gas analyzer is HORIBA MMA-500 and can measure the SO<sub>2</sub>, NO<sub>x</sub> and O<sub>2</sub> concentration in the flue gas continuously. It can work within the following range

|                       |         |          |          |
|-----------------------|---------|----------|----------|
| SO <sub>2</sub> (ppm) | 0.1-500 | 0.1-1000 | 0.1-2000 |
| NO <sub>x</sub> (ppm) | 0.1-500 | 0.1-1000 | 0.1-2000 |
| O <sub>2</sub> (%)    | 0.01-10 | 0.01-25  | —        |

Table 1 is the analyses of the oil shale tested

Table 1 (weight %)

Ultimate fuel analysis (%)

| C     | H    | S <sub>q</sub> | N    | O    | (CO <sub>2</sub> ) <sub>k</sub> |
|-------|------|----------------|------|------|---------------------------------|
| 11.58 | 1.27 | 1.42           | 0.49 | 0.56 | 11.6                            |

\* S<sub>q</sub> is the total sulphur

Ash analysis (%)

| SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO  | CaO   | K <sub>2</sub> O | Na <sub>2</sub> O | SO <sub>3</sub> | P <sub>2</sub> O <sub>5</sub> |
|------------------|--------------------------------|--------------------------------|------|-------|------------------|-------------------|-----------------|-------------------------------|
| 42.1             | 11.17                          | 5.32                           | 1.28 | 27.72 | 1.01             | 0.55              | 1.74            | 4.6                           |

Proximate fuel analysis

| moisture(%)         | ash(%)              | volatile(%)         | char(%) | net heating value(kj/kg) |
|---------------------|---------------------|---------------------|---------|--------------------------|
| 4.62                | 60.46               | 15.42               | 11.58   | 4857                     |
| T <sub>1</sub> (°C) | T <sub>2</sub> (°C) | T <sub>3</sub> (°C) |         |                          |
| 1140                | 1160                | 1200                |         |                          |

The oil shale tested is of high sulphur, but the CaO and (CO<sub>2</sub>)k contents in its ash are also high. As a result, it should be capable of capturing sulphur by itself, when it is burnt in fluidized bed combustor. All the experiments were carried out under the following conditions,

Bed temperature (T): 800-950 C

Bed pressure drop ( $\Delta P$ ): 89-189 mmH<sub>2</sub>O

Excess air coefficient ( $\alpha$ ): 1.14-1.46

Particle diameter ( $D_p$ ): 0.25-0.5, 0.5-1.0, 1.0-2.0, 2.0-3.0 mm

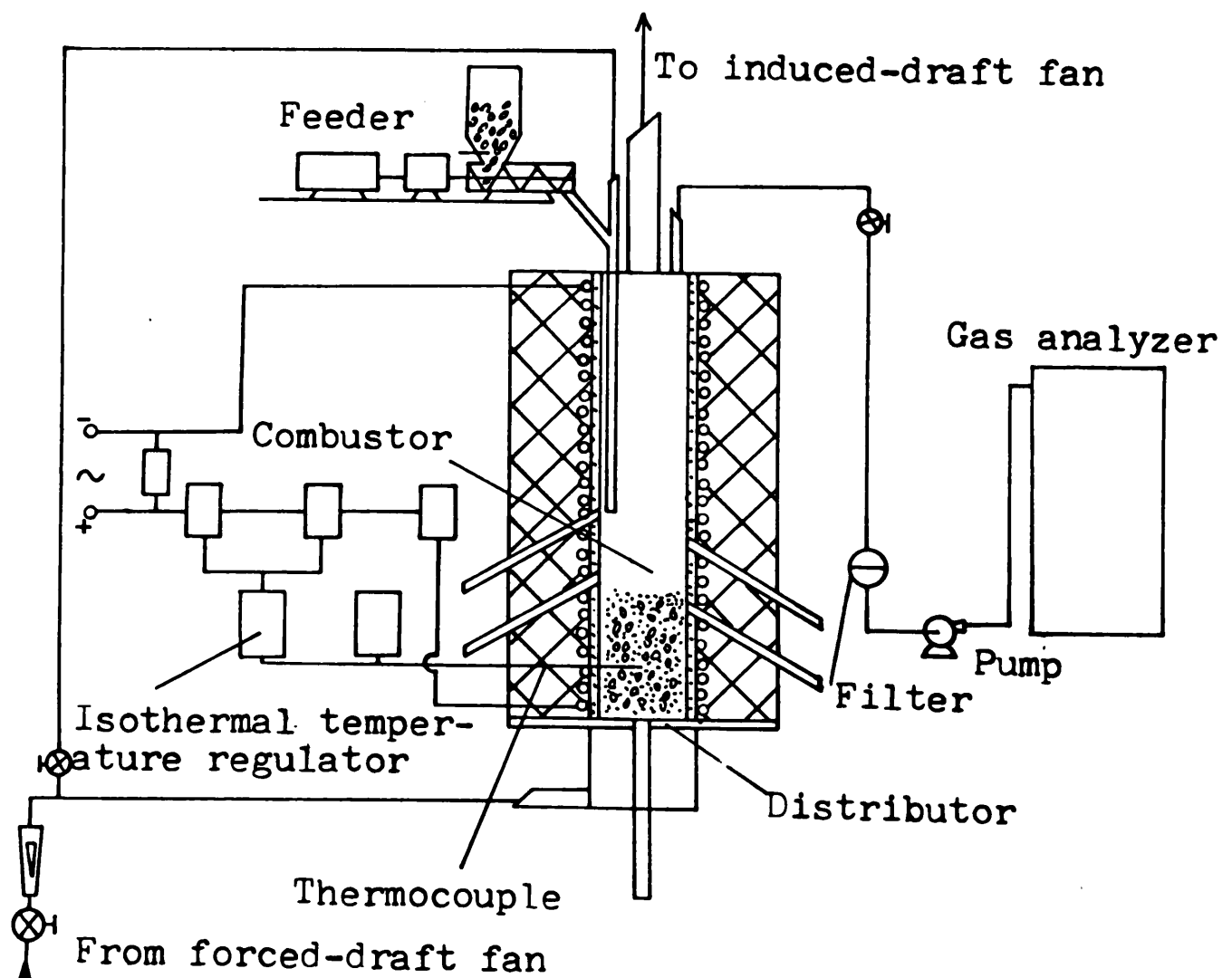


Figure 1 Schematic diagram of the experiment equipment

## 3. RESULTS

Under the above condition, the SO<sub>2</sub>, NO<sub>x</sub> and O<sub>2</sub> concentrations in the combustion products were measured and the value of the self-sulphur-retention ( $\eta_{SO_2}$ ) were calculated on the basis of the following equation.

$$\eta_{SO_2} = 1 - \frac{V_{gy} C_{SO_2}}{K \psi B S_q} \quad (1)$$

where,

B, Oil shale consumption

V<sub>gy</sub>, Volume of dry flue gases

C<sub>SO<sub>2</sub></sub>, SO<sub>2</sub> concentration in flue gases

K, Reaction coefficient (K=2)

$\psi$ , Ratio of volatile sulphur to total sulphur. According to the rules of coal analysis edited by the Chinese academy of coal science, the difference between volatile sulphur and total sulphur is negligible when  $S_q < 2\%$ , so in this case,  $\psi = 1$ .

The excess air coefficient was evaluated during the measurement by following correlation,

$$\alpha \approx \frac{21}{21 - O_2} \quad (2)$$

The measured results are as follows,

(1) The effect of bed temperature (T) on sulphur retention ( $\eta_{SO_2}$ )

Experimental conditions,

Particle diameter,  $D_p = 0.25 - 0.5$  mm

Superficial gas velocity,  $W = 0.53$  m/s

Bed pressure drop,  $\Delta P = 189$  mmH<sub>2</sub>O (or bed height  $H = 230$  mm)

Excess air coefficient,  $\alpha = 1.2$

The data averaged over thirty measurements are given in table 2

Table 2

|  |          |          |          |          |
|--|----------|----------|----------|----------|
| Bed temperature (T) °C                               | 800 ± 10 | 850 ± 10 | 900 ± 10 | 950 ± 10 |
| SO <sub>2</sub> concentration (SO <sub>2</sub> ) ppm | 389.9    | 365.12   | 723.86   | 1668.03  |
| NO <sub>x</sub> concentration (NO <sub>x</sub> ) ppm | 209.52   | 264.29   | 124.29   | 149.59   |
| Sulphur retention ( $\eta_{SO_2}$ ) %                | 96.84    | 97.04    | 94.12    | 86.45    |

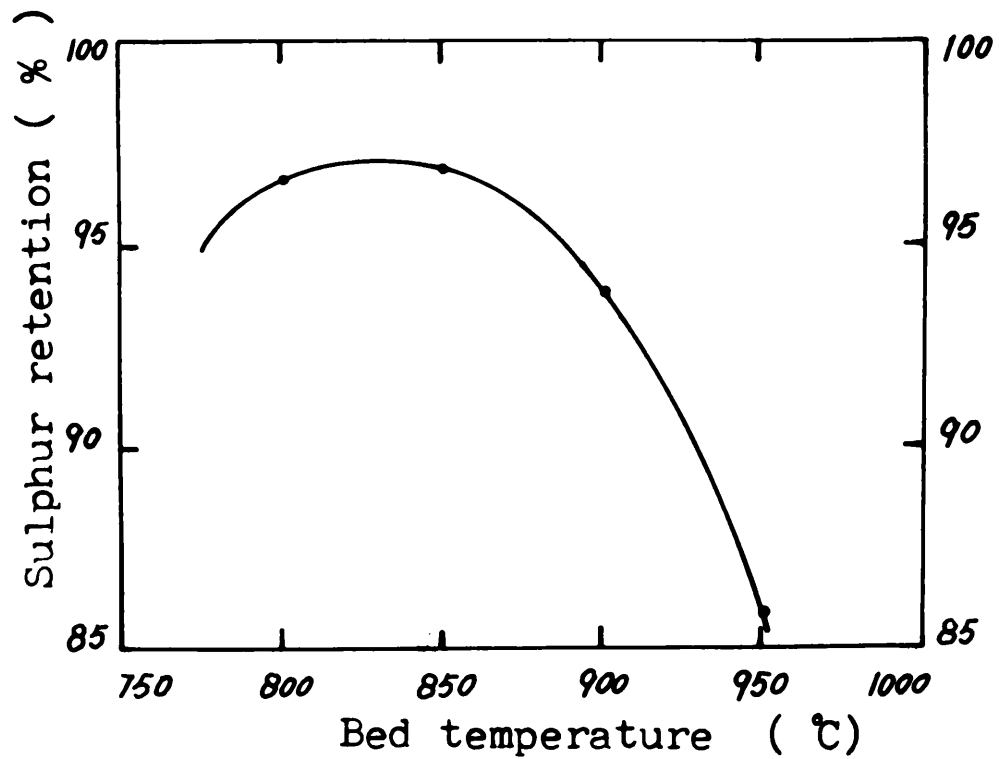


Figure 2 Effect of bed temperature on sulphur retention

(2) The effect of excess air coefficient ( $\alpha$ ) on sulphur retention ( $\eta_{SO_2}$ )

Experimental conditions ;

Particle diameter,  $D_p=0.25-0.5$  mm

Superficial gas velocity,  $W=0.53$  m/s

Bed pressure drop,  $\Delta P=189$  mmH<sub>2</sub>O

Bed temperature,  $T=850 \pm 10$  °C

Table 3 shows the data averaged over thirty measurements

Table 3

|  |        |        |        |       |        |
|--|--------|--------|--------|-------|--------|
| Excess air coefficient ( $\alpha$ )                  | 1.14   | 1.18   | 1.21   | 1.3   | 1.46   |
| SO <sub>2</sub> concentration (SO <sub>2</sub> ) ppm | 547.43 | 499.77 | 362.29 | 332.5 | 218.13 |
| NO <sub>x</sub> concentration (NO <sub>x</sub> ) ppm | 235.29 | 215.62 | 239    | 248   | 268.64 |
| Sulphur retention ( $\eta_{SO_2}$ ) %                | 95.76  | 96     | 97.04  | 97.09 | 97.87  |

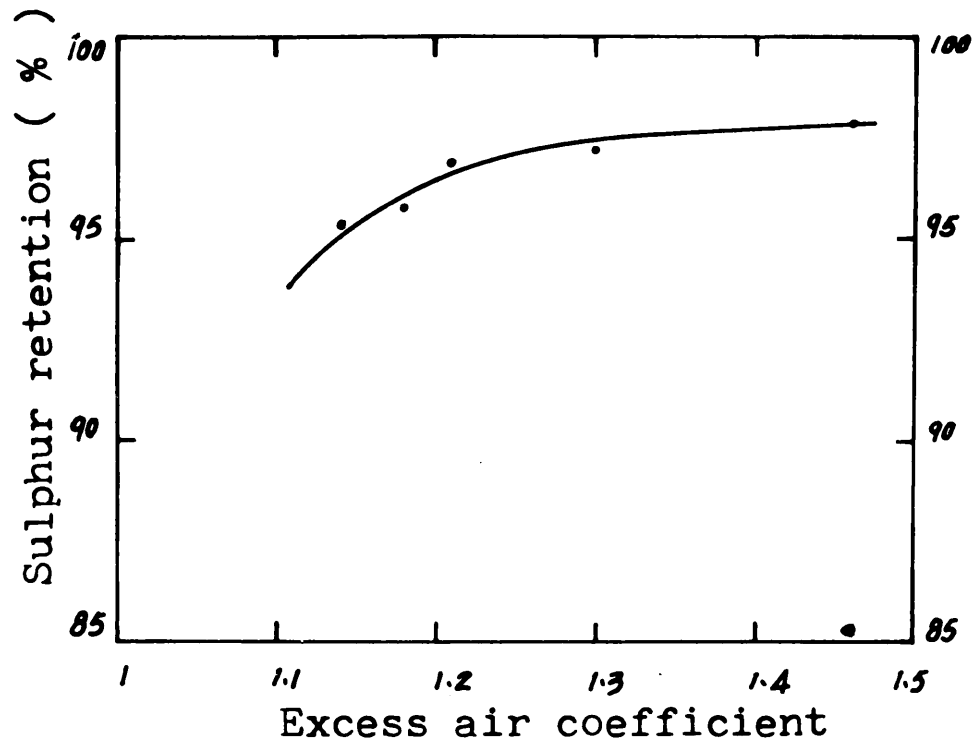


Figure 3 Effect of excess air coefficient on sulphur retention

(3) The effect of bed pressure drop ( $\Delta P$ ) on sulphur retention ( $\eta_{SO_2}$ )

Experimental conditions,

Particle diameter,  $D_p = 0.25 - 0.5$  mm

Superficial gas velocity,  $W = 0.53$  m/s

Excess air coefficient,  $\alpha = 1.2$  Bed temperature,  $T = 850 \pm 10$  °C

Table 4 is the data averaged over thirty measurements

Table 4

|  |        |        |        |        |
|--|--------|--------|--------|--------|
| Bed pressure drop ( $\Delta P$ ) mmH <sub>2</sub> O  | 89     | 129    | 159    | 189    |
| SO <sub>2</sub> concentration (SO <sub>2</sub> ) ppm | 115.82 | 252.74 | 341.97 | 365.12 |
| NO <sub>x</sub> concentration (NO <sub>x</sub> ) ppm | 238.78 | 192.86 | 240.30 | 264.29 |
| Sulphur retention ( $\eta_{SO_2}$ ) %                | 99.06  | 97.95  | 97.22  | 97.04  |

(4) The effect of mean particle diameter ( $D_p$ ) on sulphur retention

Experimental conditions,

Bed height,  $H = 192$  mm

Excess air coefficient,  $\alpha = 1.2$

Bed temperature,  $T = 850 \pm 10$  °C

The data averaged over thirty measurements are shown in table 5

Table 5

|  |          |         |         |         |
|--|----------|---------|---------|---------|
| Sieve size (Dp) mm                                   | 0.25-0.5 | 0.5-1.0 | 1.0-2.0 | 2.0-3.0 |
| Mean particle diameter (Dp) mm                       | 0.375    | 0.75    | 1.5     | 2.5     |
| Bed pressure drop( $\Delta P$ ) mmH <sub>2</sub> O   | 159      | 159     | 154     | 141.5   |
| SO <sub>2</sub> concentration (SO <sub>2</sub> ) ppm | 341.97   | 172.32  | 117.67  | 559.35  |
| NO <sub>x</sub> concentration (NO <sub>x</sub> ) ppm | 240.35   | 272.23  | 317.93  | 437.68  |
| Sulphur retention ( $\eta_{SO_2}$ ) %                | 97.22    | 98.6    | 99.04   | 95.46   |

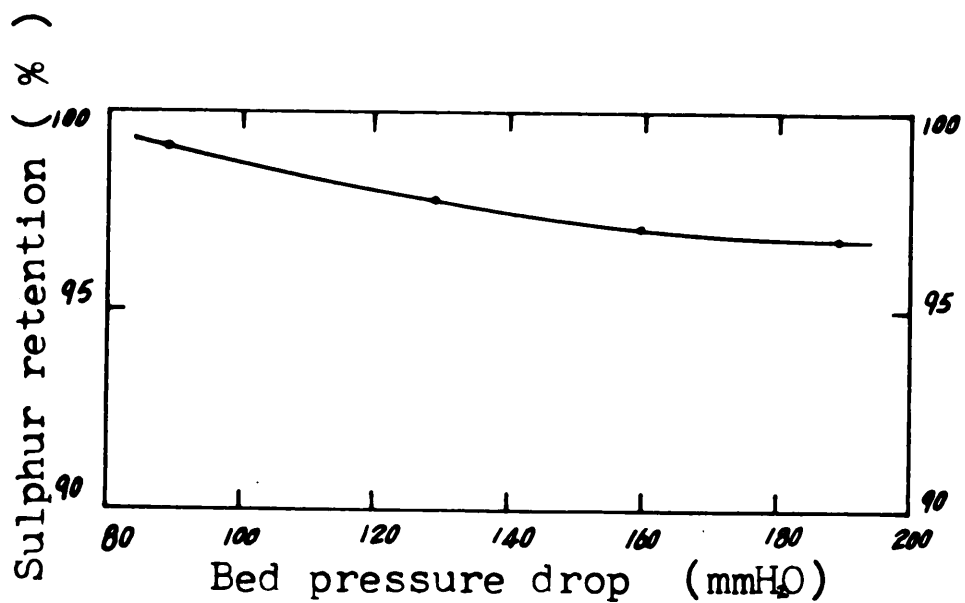


Figure 4 Effect of bed pressure drop on sulphur retention

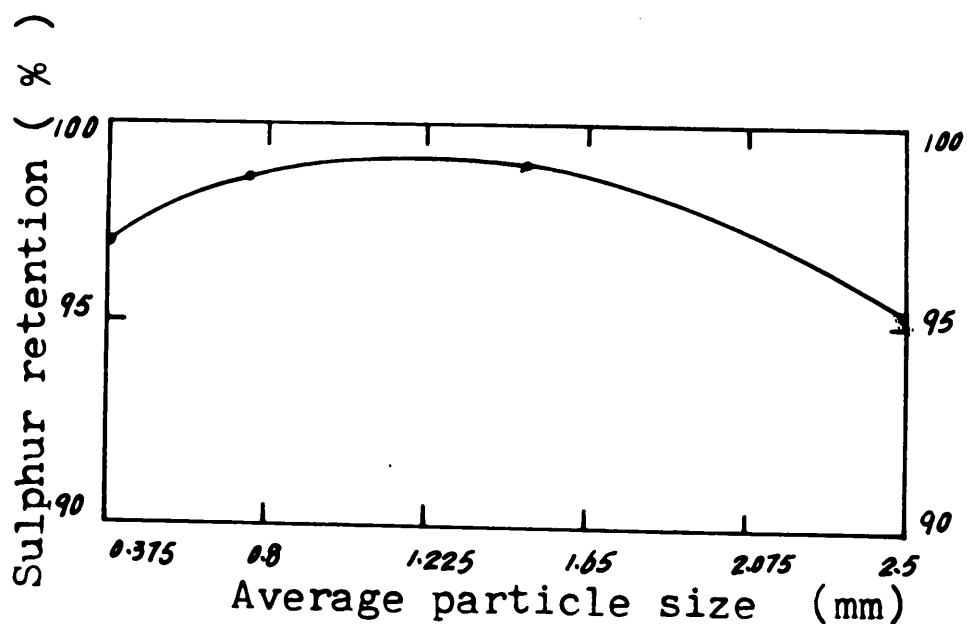


Figure 5 Effect of average particle size on sulphur retention

The experiments with wide size distribution of oil shale particle ( $D_p=0.5-3.0$  mm) were done under following conditions,

Bed temperature ,  $T=850\pm 10$  °C

Superficial gas velocity ,  $W=1.39$  m/s

Excess air coefficient ,  $\alpha=1.2$

Bed pressure drop ,  $\Delta P=132$  mmH<sub>2</sub>O (or bed height  $H=192.5$  mm )

The measured results are

SO<sub>2</sub> concentration,  $SO_2=207.32$  ppm

NO<sub>x</sub> concentration ,  $NO_x=355$  ppm

Sulphur retention ,  $\eta_{so_2}=98.32$  %

#### 4 CONCLUSIONS

(1) Oil shale with high sulphur, high CaO and a low net heating value can desulphurate effectively without adding limestone or other sorbents in fluidized bed combustor. Under various conditions, the minimal sulphur retention is 86% and the maximum of sulphur retention can reach 99% .

(2) Among the operating parameters, sulphur retention has been found to be the most sensitive to the bed temperature. The optimal bed temperature is 850°C. As the bed temperature increases, the sulphur retention goes up at first and reaches its maximum at 850°C, then decreases. the other operating parameters have very small influences on the sulphur retention

(3) This kind of oil shale can be used as the fuel of fluidized bed boiler.

#### 5. REFERENCES

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