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LABORATORY EXPERIMENTS AND MATHEMATICAL MODELLING OF OIL SHALE FLUIDIZED COMBUSTION AND SULFUR DIOXIDE EVOLUTION

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This paper describes the laboratory experiments and mathematical modelling on oil shale batch fluidized combustion. The mathematical model developed is a kind of progressive diffusion and reaction model, including mass and heat transfer during combustion and sulfur dioxide formation and capture reactions. The results calculated using the model fit well the experimental data.

Experimental

A laboratory apparatus with a sulfur dioxide analyzer on the exhaust line was designed and built for investigating batch fluidized-bed combustion of oil shale.

Sixteen experimental runs were made for Maoming oil shale. The batch process parameters were: oil shale size 0.5-1.0 mm, 1.0-2.0 mm, 2.0-3.0 mm, 3.0-5.0 mm; bed temperature 750 °C, 800 °C, 850 °C, 900 °C; moisture of oil shale: 0 %, 4 %, 8 %, 12 %; calcium carbonate added with the Ca/S molar ratio 0.0, 1.5, 3.0, 4.0; ash was added with the ash/shale weight ratio 0.0, 0.2, 0.4, 0.6. The changes in sulfur dioxide concentration in exhaust gas during combustion (residence time of oil shale) for some typical experiments are shown in Fig. 1*a-e* (dotted lines indicating the experiment results).

It is shown that in all experiments a large part of sulfur in oil shale has been already burnt out and converted into sulfur dioxide within 40 seconds, while the peak concentration of sulfur dioxide varies from about 100 to 200 ppm. Sulfur dioxide concentration gradually decreases to zero during about 80-90 seconds.

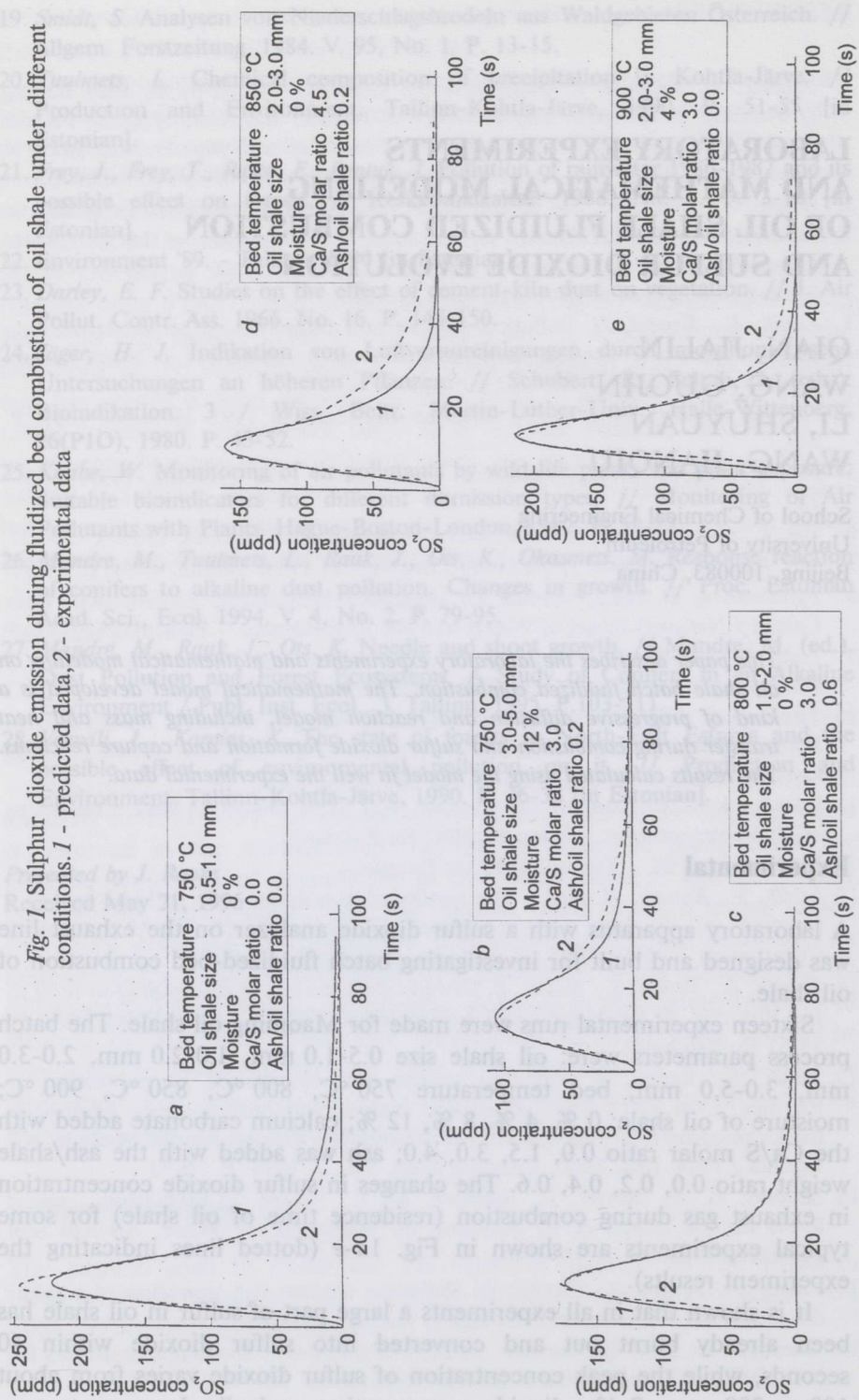

Fig. 1. Sulphur dioxide emission during fluidized bed combustion of oil shale under different conditions. *1* - predicted data, *2* - experimental data

Mathematical Modelling

A mathematical model for oil shale combustion and sulfur dioxide emission was developed. It includes energy equations for oil shale pyrolysis, combustion of its volatile matter and shale char, mass equations for oxygen diffusion into the particle and consumption, sulfur dioxide diffusion from the particle, reaction of a part of sulfur dioxide with CaO in the particle and capture of another part of sulfur dioxide by added $CaCO_3$ and shale ash.

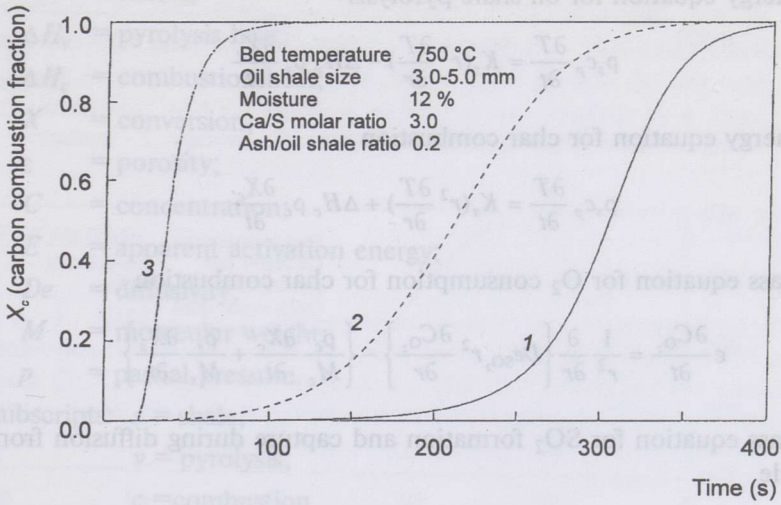

Fig. 2. Organic carbon combustion profiles in oil shale char particle. *1* - center, *2* - half radius, *3* - surface

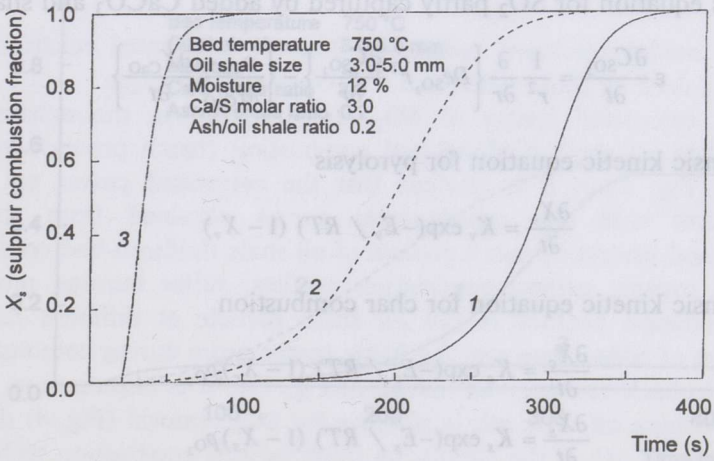

Fig. 3. Sulphur burning profiles in oil shale char particle. *1* - center, *2* - half radius, *3* - surface

The intrinsic oil shale pyrolysis kinetics, the intrinsic shale char combustion kinetics and SO_2 formation kinetics are included in the model, as well as the heat of shale pyrolysis and heat of char combustion. The temperature rise due to the rapid combustion of volatiles was calculated and its effect on the pyrolysis of oil shale was also considered.

The model developed belongs to the progressive diffusion and reaction model. It is rather universal in comparison with the shrinking core model and uniform reaction model [1, 2].

The mathematical expressions are shown as follows:

Energy equation for oil shale pyrolysis

$$\rho_s c_p \frac{\partial T}{\partial t} = K_s (r^2 \frac{\partial T}{\partial r}) - \Delta H_v \rho_v \frac{\partial X_v}{\partial t} \tag{1}$$

Energy equation for char combustion

$$\rho_s c_p \frac{\partial T}{\partial t} = K_s (r^2 \frac{\partial T}{\partial r}) + \Delta H_c \rho_c \frac{\partial X_c}{\partial t} \tag{2}$$

Mass equation for O_2 consumption for char combustion

$$\varepsilon \frac{\partial C_{O_2}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ De_{SO_2} r^2 \frac{\partial C_{O_2}}{\partial r} \right\} - \left\{ \frac{\rho_c}{M_c} \frac{\partial X_c}{\partial t} + \frac{\rho_s}{M_s} \frac{\partial X_s}{\partial t} \right\} \tag{3}$$

Mass equation for SO_2 formation and capture during diffusion from the particle

$$\varepsilon \frac{\partial C_{SO_2}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ De_{SO_2} r^2 \frac{\partial C_{SO_2}}{\partial r} \right\} + \left\{ \frac{\rho_s}{M_s} \frac{\partial X_s}{\partial t} - \frac{\rho_{CaO}}{M_{CaO}} \frac{\partial X_{CaO}}{\partial t} \right\} \tag{4}$$

Mass equation for SO_2 partly captured by added $CaCO_3$ and shale ash

$$\varepsilon \frac{\partial C_{SO_2}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ De_{SO_2} r^2 \frac{\partial C_{SO_2}}{\partial r} \right\} - \left\{ \frac{\rho_{CaO}}{M_{CaO}} \frac{\partial X_{CaO}}{\partial t} \right\} \tag{5}$$

Intrinsic kinetic equation for pyrolysis

$$\frac{\partial X_v}{\partial t} = K_v \exp(-E_v / RT)\ (1 - X_v) \tag{6}$$

Intrinsic kinetic equation for char combustion

$$\frac{\partial X_c}{\partial t} = K_c \exp(-E_c / RT)\ (1 - X_c) p_{O_2} \tag{7}$$

$$\frac{\partial X_s}{\partial t} = K_s \exp(-E_s / RT)\ (1 - X_s) p_{O_2} \tag{8}$$

$$\frac{\partial X_{CaO}}{\partial t} = K_{CaO} \exp(-E_{CaO} / RT)(1 - X_{CaO}) p_{SO_2} \tag{9}$$

where ρ = density;

c_p = heat capacity;

T = temperature;

t = time;

K = thermal conductivity;

r = radius;

ΔH_v = pyrolysis heat;

ΔH_c = combustion heat;

X = conversion;

ε = porosity;

C = concentration;

E = apparent activation energy;

De = diffusivity;

M = molecular weight;

p = partial pressure.

The subscripts: s = shale;

v = pyrolysis;

c =combustion.

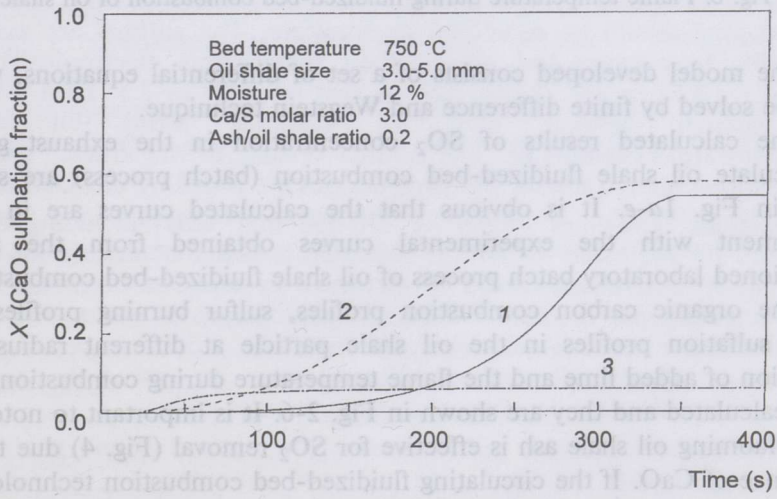

Fig. 4. CaO sulphation profiles in oil shale char particle. *1* - center, *2* - half radius, *3* - surface

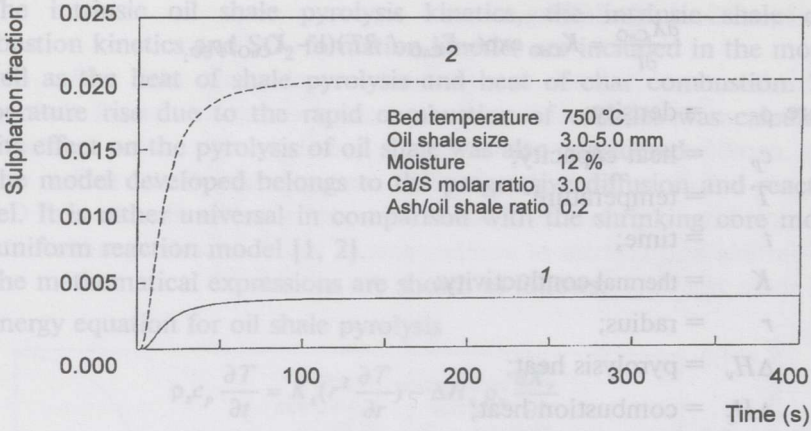

Fig. 5. Lime sulphation fraction vs time. *1* - average, *2* - surface

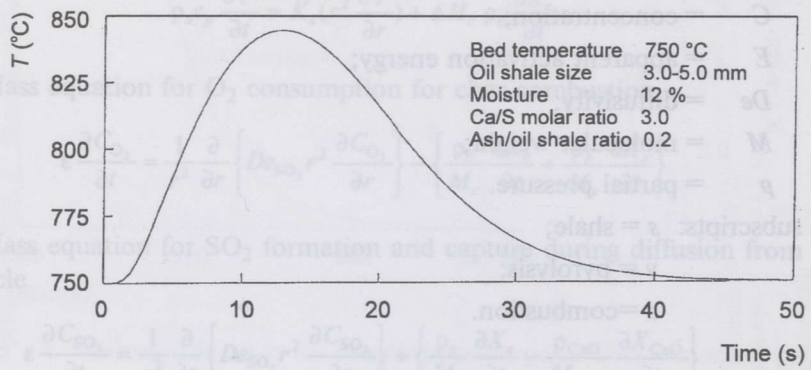

Fig. 6. Flame temperature during fluidized-bed combustion of oil shale

The model developed consists of a set of differential equations, which can be solved by finite difference and Wegstein technique.

The calculated results of SO_2 concentration in the exhaust gas at particulate oil shale fluidized-bed combustion (batch process) are shown also in Fig. 1*a-e*. It is obvious that the calculated curves are in good agreement with the experimental curves obtained from the above mentioned laboratory batch process of oil shale fluidized-bed combustion.

The organic carbon combustion profiles, sulfur burning profiles and CaO sulfation profiles in the oil shale particle at different radius, the sulfation of added lime and the flame temperature during combustion were also calculated and they are shown in Fig. 2-6. It is important to note that the Maoming oil shale ash is effective for SO_2 removal (Fig. 4) due to the presence of CaO. If the circulating fluidized-bed combustion technology is used in a power plant, the SO_2 emission can be greatly reduced due to the sulfation of CaO in ash. Certainly, an optimum ratio of ash to feed is to be

determined for commercial continuos operation and additional $CaCO_3$ may not be needed. The model can be used to solve this problem by coupling with the oil shale residence time distribution function for different sizes of the feed.

Conclusion

A laboratory apparatus was designed and built for particulate oil shale batch fluidized combustion. An appropriate combustion model was developed. The calculated sulfur dioxide concentrations are in good agreement with experimental data. Oil shale fluidized combustion technology is promising due to the advantages of less fly ash and sulfur dioxide emission, and oil shale is economically feasible as a local boiler fuel.

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