

# CARBON DIOXIDE BINDING IN THE HETEROGENEOUS SYSTEMS FORMED AT COMBUSTION OF OIL SHALE. 2. INTERACTIONS OF SYSTEM COMPONENTS – THERMODYNAMIC ANALYSIS

R. KUUSIK, L. TÜRN, A. TRIKKEL, M. UIBU

Tallinn Technical University,  
Institute of Basic and Applied Chemistry  
5 Ehitajate St., Tallinn 19086, Estonia

*SO<sub>2</sub> and CO<sub>2</sub> are essential components of the flue gases formed at oil shale combustion. The first of them is a precursor of acid rain; the other one causes greenhouse effect. In the present work the reactions occurring in the presence of these components in the systems of flue gas – oil shale ash (gas – solid) and flue gas – ash pulp (gas – solid – liquid) were studied. Thermodynamic calculations were carried out using the target-oriented HSC software.*

*In the case of the first system the changes in the equilibrium content of the components formed in the reactions between flue gas and fly ash along the gas tract in the temperature range of 1400 to 25 °C were calculated. It was found that about 13 % of the CO<sub>2</sub> formed at oil shale combustion can be bound, and that SO<sub>2</sub> and SO<sub>3</sub> can be completely bound by the end of the gas tract. Calculation of the temperature dependencies of Gibbs free energy enabled to show that carbon dioxide and sulfur dioxide can be simultaneously bound by oil shale ash in the system of flue gas – fly ash.*

*It was also shown that the equilibrium content of the components formed in the second system depends on the amount of flue gas. Ash pulp can bind, depending on the form of CaO present, up to 260 mol of CO<sub>2</sub> per m<sup>3</sup> of pulp. Dilution of the pulp does not affect the amount of CO<sub>2</sub> bound by the pulp. Water in the ponds of the ash fields can bind about 60–30 mol of CO<sub>2</sub> per m<sup>3</sup> of water, depending on whether the pond is in use or in reserve. In both cases the binding of SO<sub>2</sub> is favourable compared to the binding of CO<sub>2</sub>.*

## Introduction

The main environmentally hazardous components in the flue gases formed at oil shale combustion are sulfur dioxide SO<sub>2</sub> and carbon dioxide CO<sub>2</sub>. The first is a precursor of acid rain, the other, when accumulated in the atmosphere, causes greenhouse effect. It is predicted that already before 2100 the

content of CO<sub>2</sub> in the air will be 0.06 %, which could result in the increase in the mean temperature of the Earth by 2.5 °C or by pessimistic assumptions even by 6 °C [1].

The problem of CO<sub>2</sub> emission is quite relevant in Estonia where the annual amount of CO<sub>2</sub> released is 13.5 tons per capita [2]. The main source of CO<sub>2</sub> emission in Estonia is oil shale energetics. On the other hand, alkaline oil shale ash and its water suspension are formed at energy production, but their capability to bind these gases is evidently not realised. While SO<sub>2</sub> binding by the ash is an actual process – in the power stations working on oil shale about 75–80 % of SO<sub>2</sub> formed is bound into the solid phase [2], and several possibilities for increasing the binding efficiency have been shown [3–5], the binding of CO<sub>2</sub> by oil shale ash is quite a new topic [6, 7].

To elucidate the possibilities for reducing CO<sub>2</sub> emissions, thermodynamic analysis of the reactions occurring between the gaseous and solid combustion products formed at oil shale combustion was carried out. Certainly, thermodynamic analysis by calculating the changes in Gibbs free energy  $\Delta G_T$ , gives only an estimation of the possibilities for obtaining certain equilibrium compositions in these systems, but kinetic parameters – time necessary for reaching equilibrium and effect of activation energy were herein discarded. In this paper  $\Delta G_T$ , its temperature dependency and equilibrium composition of reaction products were calculated for a set of reactions using the HSC software [8].

Two different heterogeneous systems were studied:

- flue gas formed at oil shale combustion – oil shale ash (solid – gas)
- ash suspension (ash pulp from hydrotransport) – flue gas or air (solid – liquid – gas)

## Results and Discussion

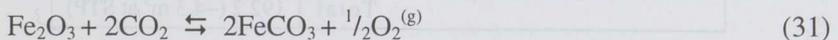
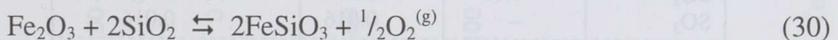
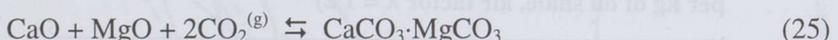
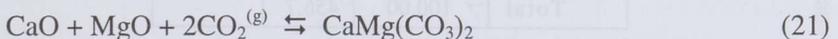
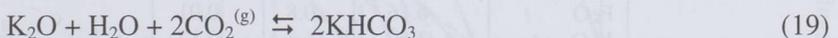
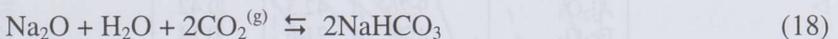
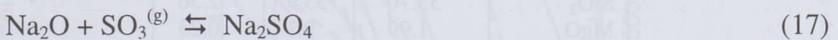
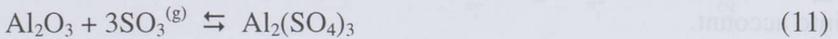
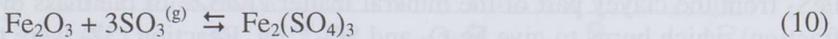
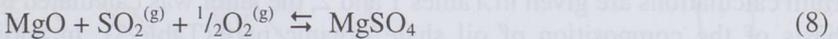
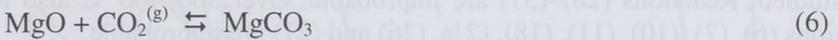
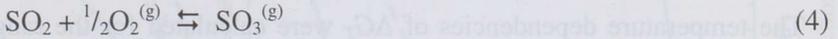
### System Flue Gas – Fly Ash

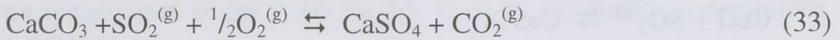
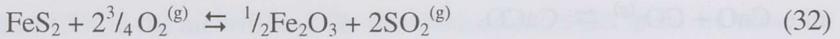
#### *Probable Reactions and Initial Composition of the Phases*

In the first approach, temperature dependencies of Gibbs free energy changes  $\Delta G_T$  were calculated for Reactions (1)–(34) in order to find out which are the most probable reaction products to be used in equilibrium calculations.

The following notation (according to HSC) was used:

- (g) for gaseous compound
- (a) for compound in solution (CO<sub>2</sub><sup>(a)</sup> – dissolved carbon dioxide)
- (+a) or (–a) for ion with +1 or –1 charge in solution
- (+2a) or (–2a) for ion with +2 or –2 charge in solution
- Without superscript – for compound in its most probable state under current conditions





The temperature dependencies of  $\Delta G_T$  were calculated for the range of 1400–25 °C (Fig. 1). It can be concluded that in the temperature interval studied, Reactions (28)–(31) are improbable. Over 300–400 °C also Reactions (6), (7), (10), (11), (18), (21), (26) and (27) are improbable.

The data on the composition of fly ash and flue gas used in the equilibrium calculations are given in Tables 1 and 2, the latter was calculated on the basis of the composition of oil shale organic part (Table 3). In addition,  $\text{CO}_2^{(\text{g})}$  from carbonates (46 % of the mass of carbonaceous fraction [2]) and  $\text{FeS}_2$  from the clayey part of the mineral matter (12.3 % of the mass of clay fraction) which burns to give  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_2^{(\text{g})}$  by Reaction (32) were taken into account.

**Table 1. Composition of Fly Ash Formed at Oil Shale Combustion\***

Component	Content, %	per kg of oil shale	
		g	mol
CaO	46.11	210.6	3.76
SiO <sub>2</sub>	33.70	153.9	2.56
MgO	1.99	9.1	0.23
Al <sub>2</sub> O <sub>3</sub>	9.26	42.3	0.42
Fe <sub>2</sub> O <sub>3</sub>	4.73	21.6	0.14
FeO	0.16	0.8	0.01
K <sub>2</sub> O	3.57	16.3	0.17
Na <sub>2</sub> O	0.46	2.1	0.034
Total	100.00	456.7	

\* Based on the data presented in [2],  
the ratio of carbonaceous : clay = 60 : 40.

**Table 2. Composition of Flue Gas Formed at Oil Shale Combustion (amounts in moles per kg of oil shale, air factor  $\lambda = 1.2$ )**

Component	From organic part	From mineral part	Total
CO <sub>2</sub>	22.59	3.92	26.51
H <sub>2</sub> O	16.98	–	16.98
N <sub>2</sub>	136.70	5.08	141.78
O <sub>2</sub>	6.04	0.22	6.26
SO <sub>2</sub>	0.19	0.54	0.72 (~10.7 g/m <sup>3</sup> )
SO <sub>3</sub>	–	0.016	0.016
Total			192.2 (~4.3 m <sup>3</sup> at STP)

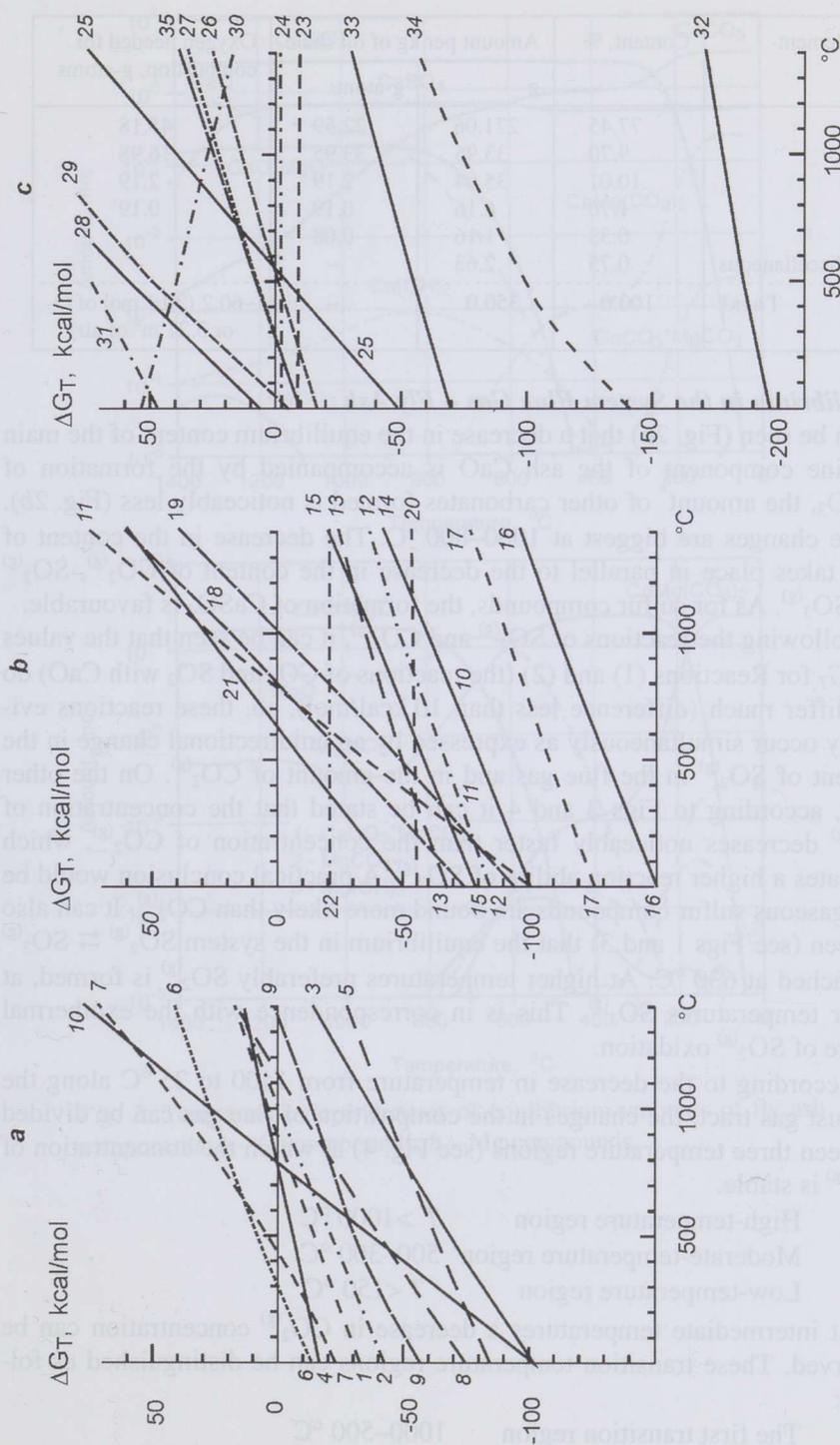


Fig. 1. Temperature dependencies of Gibbs free energy changes  $\Delta G_T$ : a - Reactions (1)-(10); b - Reactions (11)-(22); c - Reactions (23)-(35)

Table 3. Composition of Oil Shale Organic Part (35 % of oil shale [4])

Element	Content, %	Amount per kg of oil shale		Oxygen needed for combustion, g-atoms
		g	g-atoms	
C	77.45	271.06	22.59	45.18
H	9.70	33.95	33.95	16.98
O	10.01	35.04	2.19	- 2.19
S	1.76	6.16	0.19	0.19
N	0.33	1.16	0.08	-
Miscellaneous	0.75	2.63	-	-
Total	100.0	350.0	-	~60.2 (30.1 mol of O <sub>2</sub> or 3.21 m <sup>3</sup> of air)

### Equilibrium in the System Flue Gas – Fly Ash

It can be seen (Fig. 2a) that a decrease in the equilibrium content of the main alkaline component of the ash CaO is accompanied by the formation of CaCO<sub>3</sub>, the amount\* of other carbonates formed is noticeably less (Fig. 2b). These changes are biggest at 1000–800 °C. The decrease in the content of CaO takes place in parallel to the decrease in the content of CO<sub>2</sub><sup>(g)</sup>, SO<sub>2</sub><sup>(g)</sup> and SO<sub>3</sub><sup>(g)</sup>. As for sulfur compounds, the formation of CaSO<sub>4</sub> is favourable.

Following the reactions of SO<sub>2</sub><sup>(g)</sup> and CO<sub>2</sub><sup>(g)</sup>, it can be seen that the values of ΔG<sub>T</sub> for Reactions (1) and (2) (the reactions of CO<sub>2</sub> and SO<sub>2</sub> with CaO) do not differ much (difference less than 10 kcal/mol), so, these reactions evidently occur simultaneously as expressed by an unidirectional change in the content of SO<sub>2</sub><sup>(g)</sup> in the flue gas and in the amount of CO<sub>2</sub><sup>(g)</sup>. On the other hand, according to Figs 3 and 4 it can be stated that the concentration of SO<sub>2</sub><sup>(g)</sup> decreases noticeably faster than the concentration of CO<sub>2</sub><sup>(g)</sup>, which indicates a higher reaction ability of SO<sub>2</sub><sup>(g)</sup>. A practical conclusion would be that gaseous sulfur compounds are bound more likely than CO<sub>2</sub><sup>(g)</sup>. It can also be seen (see Figs 1 and 3) that the equilibrium in the system SO<sub>2</sub><sup>(g)</sup> ⇌ SO<sub>3</sub><sup>(g)</sup> is reached at 630 °C. At higher temperatures preferably SO<sub>2</sub><sup>(g)</sup> is formed, at lower temperatures SO<sub>3</sub><sup>(g)</sup>. This is in correspondence with the exothermal nature of SO<sub>2</sub><sup>(g)</sup> oxidation.

According to the decrease in temperature from 1400 to 25 °C along the exhaust gas tract, the changes in the composition of flue gas can be divided between three temperature regions (see Fig. 4) at which the concentration of CO<sub>2</sub><sup>(g)</sup> is stable.

High-temperature region       $T > 1000$  °C

Moderate-temperature region      500–300 °C

Low-temperature region       $T < 150$  °C

At intermediate temperatures a decrease in CO<sub>2</sub><sup>(g)</sup> concentration can be observed. These transition temperature regions can be distinguished as follows:

The first transition region      1000–500 °C

The second transition region      300–150 °C

\* The amount in Table 4 and on Figs 2–4 is expressed in moles per kg of oil shale.

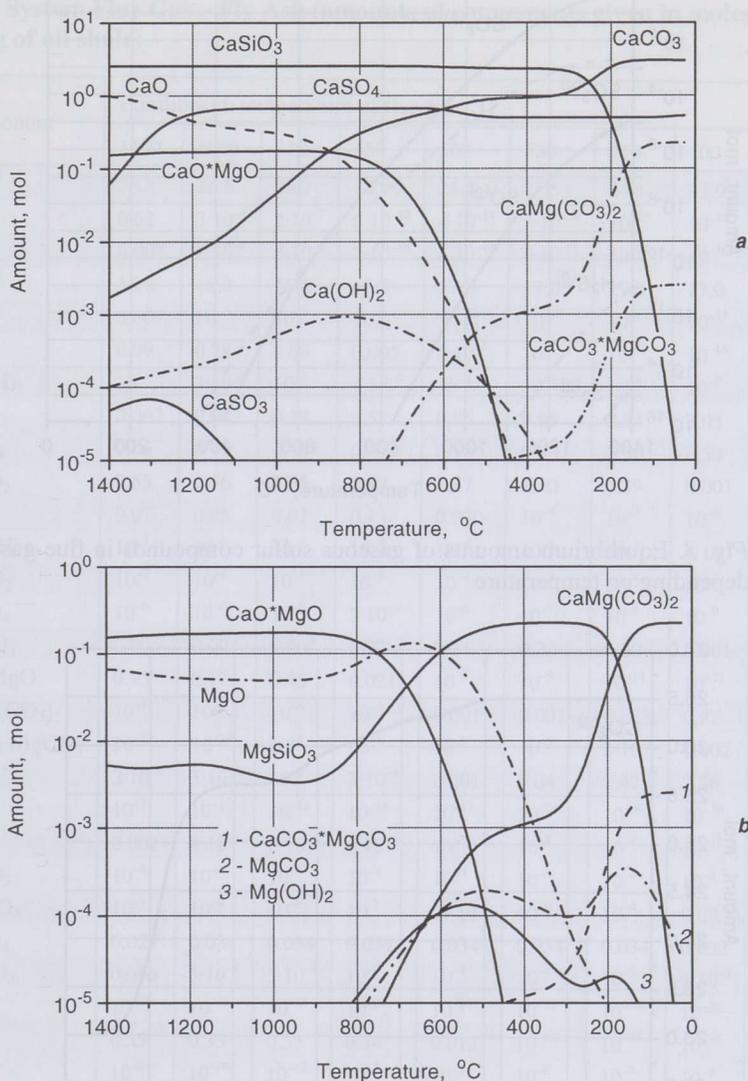


Fig. 2. Temperature dependencies of equilibrium amounts of fly ash components: a – Ca compounds; b – Mg compounds

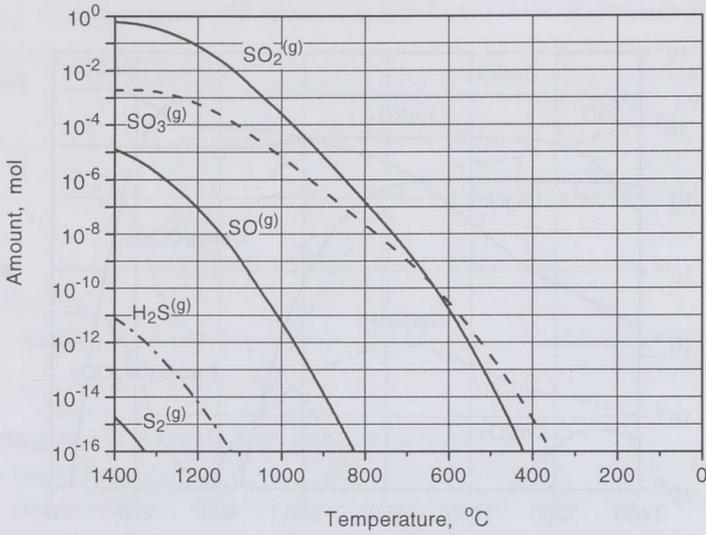


Fig. 3. Equilibrium amounts of gaseous sulfur compounds in flue gas depending on temperature

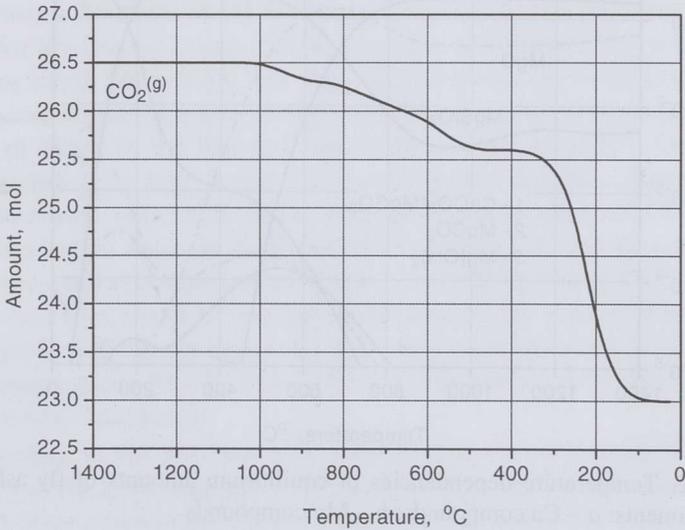


Fig. 4. Equilibrium amounts of carbon dioxide in flue gas depending on temperature



### **High-Temperature Region ( $T > 1000$ °C)**

In this temperature region the equilibrium amount of  $\text{CO}_2^{(g)}$  in the flue gas is on the level of 26.5–26.2 moles per kg of oil shale (see Table 4). Almost a half of the initial CaO is utilized to give secondary  $\text{CaSiO}_3$  in the reaction with  $\text{SiO}_2$ . Among Ca compounds,  $\text{CaSiO}_3$  and CaO prevail. Amount of  $\text{CaCO}_3$  is low, but increases from  $10^{-3}$  to 0.1 mol/kg with decreasing temperature. Much calcium is utilized in binding gaseous sulfur compounds; the main product formed is  $\text{CaSO}_4$ . Part of MgO reacts with  $\text{SiO}_2$  to give  $\text{MgSiO}_3$ , and another part with CaO to give  $\text{CaO} \cdot \text{MgO}$ . The amount of  $\text{MgCO}_3$  is low.  $\text{SiO}_2$  is completely utilized in forming secondary Ca and Mg silicates.

At higher temperatures of this region, the amount of  $\text{SO}_2^{(g)}$  formed is relatively high – 0.62 mol/kg (concentration in the flue gas  $\sim 9$  g/m<sup>3</sup>). At temperatures near 1000 °C it decreases to  $3 \cdot 10^{-4}$  mol/kg (concentration  $\sim 6$  mg/m<sup>3</sup>). The amount of  $\text{SO}_3^{(g)}$  is some magnitudes lower. So, in this temperature region the amount of free sulfur compounds increases rapidly with the increase in temperature, at lower temperatures they are mainly bound into calcium sulfate. The amount of other sulfates is low.

### **The First Transition Region (1000–500 °C)**

This region is characterized by a slow decrease in  $\text{CO}_2^{(g)}$  amount from 26.5 to 25.6 mol/kg (see Fig. 4), accompanied by a decrease in the amount of  $\text{CaO} \cdot \text{MgO}$  and an increase in the amount of  $\text{CaCO}_3$ . The amount of free CaO decreases from 0.28 to  $5 \cdot 10^{-5}$  mol/kg, the formation of complex carbonates starts, and the amount of free MgO increases by some tens of percent. The amount of  $\text{MgSiO}_3$  increases and reaches its maximum level (see Fig. 2b). The amount of  $\text{CaSiO}_3$  remains practically unchangeable. The amount of  $\text{CaSO}_4$  falls to its final level.

The amount of free  $\text{SO}_2^{(g)}$  drops to  $4 \cdot 10^{-14}$  mol/kg ( $\sim 6$  mg/m<sup>3</sup>), the amount of free  $\text{SO}_3^{(g)}$  is on the same level (see Fig. 3).

### **Moderate Temperature Region (500–300 °C)**

The amount of  $\text{CO}_2^{(g)}$  is steady (25.6–25.5 mol/kg). The formation of  $\text{CaMg}(\text{CO}_3)_2$  continues and, therefore, the amount of free MgO decreases by even more than three magnitudes.

The amount of  $\text{CaSiO}_3$  is steady as well, and starts to decrease at a further decrease in temperature. As compared to silicates, carbonates and sulfates are thermodynamically more stable in this temperature region.

A certain redistribution of sulfur occurs at these temperatures – the amount of  $\text{K}_2\text{SO}_4$  increases and of other sulfates decreases. The amount of  $\text{K}_2\text{SO}_4$  reaches its maximum level, whilst the amount of  $\text{Na}_2\text{SO}_4$  drops.

### **The Second Transition Region (300–150 °C)**

A considerable decrease in  $\text{CO}_2^{(g)}$  amount from 25.5 to almost the final level 23.1 mol/kg takes place. It is due to a more intensive formation of  $\text{CaCO}_3$  accompanied by a decrease in the amount of CaO,  $\text{CaO} \cdot \text{MgO}$  and, especially, MgO. The amounts of free CaO and MgO decrease to the level of

about  $10^{-13}$  and  $10^{-6}$ , respectively. A noticeable formation of complex carbonates, mainly  $\text{CaMg}(\text{CO}_3)_2$ , starts, but its amount is still one-two magnitudes less than that of  $\text{CaCO}_3$ . Besides, some  $\text{CaCO}_3 \cdot \text{MgCO}_3$  is formed.

The formation of  $\text{KHCO}_3$  and  $\text{NaHCO}_3$  starts, but their amount is still negligible, the amounts of  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  remain unchangeable.

### **Low-Temperature Region (150–25 °C)**

At temperatures below 150 °C, the amount of  $\text{CO}_2^{(g)}$  in flue gas remains constant (23.1–23.0 mol/kg). The amounts of all carbonates reach their maximum level. However, a certain increase in the amount of Na and K bicarbonates can take place accompanied by a decrease in the amount of their carbonates. Free oxides and hydroxides are completely utilized. The secondary silicates are decomposed, the prevailing Si compound is  $\text{SiO}_2$ . At temperatures below 100 °C water vapour begins to condense and processes characteristic to ash hydroseparation could start.

The binding of  $\text{CO}_2^{(g)}$  can occur up to room temperature. All together,  $26.5 - 23.0 = 3.5$  moles of  $\text{CO}_2^{(g)}$  per kg of oil shale is bound, or the  $\text{CO}_2$  emissions could be reduced by 13.2 %. Practically, the equilibrium state is not achieved and only the amount of free CaO (~50 % of total CaO content) can be considered in these estimations.

### **Binding of Gaseous Sulfur Compounds**

Gaseous sulfur compounds  $\text{SO}_2^{(g)}$  and  $\text{SO}_3^{(g)}$  formed at oil shale combustion should be completely bound when the flue gas temperature decreases to 450 °C. The main products are  $\text{CaSO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  which bind about 0.57, 0.17 and 0.004 moles of  $\text{SO}_x^{(g)}$  per kg of oil shale, respectively (the initial amount being 0.74 mol/kg). The amount of  $\text{MgSO}_4$  formed is five-six magnitudes lower.

## **Water-Containing Systems**

### **Equilibrium at Ash Hydroseparation; the System Ash Pulp – Air**

In practice, the ash pulp is in contact with the air or the air can be bubbled through the pulp. The calculations are carried out provided that:

- Ash composition before the contact with water is the same as that of fly ash (see Table 2). CaO amount given in Table 5 is calculated on the basis of free CaO. Bound Ca is considered the inert part of the ash and is given under subset “Miscellaneous”
- Mass ratio of ash : water is 1 : 17.5
- The compounds considered to be the most probable products according to the previous calculations, besides, characteristic species in solution:  $\text{Ca}^{(+2a)}$ ,  $\text{Mg}^{(+2a)}$ ,  $\text{Na}^{(+a)}$ ,  $\text{K}^{(+a)}$ ,  $\text{H}_2\text{CO}_3^{(a)}$ ,  $\text{HCO}_3^{(-a)}$ ,  $\text{CO}_2^{(-2a)}$ ,  $\text{OH}^{(-a)}$  take part in the reactions
- The components of the air  $\text{N}_2^{(g)}$ ,  $\text{O}_2^{(g)}$ ,  $\text{CO}_2^{(g)}$ ,  $\text{CO}^{(g)}$  are considered in the calculations

In the calculations a factor  $k$  (Table 6) was used to describe the mole ratio of  $\text{CO}_2^{(g)}$  contacted with the pulp and free CaO present in the initial pulp.

According to Table 6, all the  $\text{CO}_2^{(g)}$  is bound up to the value of  $k = 1.05$ , further on the degree of  $\text{CO}_2^{(g)}$  binding decreases and  $\text{CO}_2^{(g)}$  content of the gas phase increases. When  $k$  approaches  $k \approx 1$  (Fig. 5a,b), the formation of complex carbonate  $\text{CaMg}(\text{CO}_3)_2$  starts in addition to the formation of  $\text{CaCO}_3$ . At  $k \approx 1.1$  Mg is completely bound as  $\text{CaMg}(\text{CO}_3)_2$ . Saturation of the pulp with  $\text{CO}_2^{(g)}$  is achieved on the level of  $k \approx 1.15$ , at that 90 % of calcium is bound into  $\text{CaCO}_3$  and 10 % occurs as  $\text{CaMg}(\text{CO}_3)_2$ .

**Table 5. Amounts of Ash Components, Contacted with Liquid Phase at Ash Hydroseparation**

Component	Content	
	%	moles per $\text{m}^3$ of pulp
CaO	23.6	227.5
$\text{SiO}_2$	24.0	275.9
$\text{Al}_2\text{O}_3$	7.0	37.11
$\text{Fe}_2\text{O}_3$	5.0	16.93
MgO	2.0	46.94
$\text{K}_2\text{O}$	2.0	15.64
$\text{Na}_2\text{O}$	0.1	0.87
$\text{CaSO}_4$	5.5	21.84
$\text{CaCO}_3$	5.5	29.70
Miscellaneous	23.83	—

**Table 6. Dependence of  $\text{CO}_2^{(g)}$  Binding on  $\text{CO}_2^{(g)}$  Added**

$k$	0.035	0.5	0.9	1.05	1.15	1.45	2.1	3.1
$\text{CO}_2^{(g)}$ in gas phase <sup>*1</sup>	$10^{-12}$	$3 \cdot 10^{-7}$	$10^{-6}$	$3 \cdot 10^{-6}$	0.015	0.3	0.95	1.94
$\text{CO}_2^{(g)}$ bound <sup>*2</sup>	0.035	0.5	0.9	1.05	1.135	1.15	1.15	1.16
$\text{CO}_2^{(g)}$ bound, % <sup>*3</sup>	100.0	100.0	100.0	100.0	98.7	79.3	54.8	37.4
pH	13	12	11.5	10.4	9.8	9.3	8.9	8.1

\*1 – residual equilibrium amount in flue gas after contact with ash pulp.

\*2 – amount of  $\text{CO}_2^{(g)}$  bound by pulp.

\*3 – amount of  $\text{CO}_2^{(g)}$  bound in percent from total.

Additional binding of  $\text{CO}_2^{(g)}$  is achieved due to its dissolution in aqueous phase of the pulp (Fig. 5c) with the formation of  $\text{H}_2\text{CO}_3$  and its dissociation products  $\text{HCO}_3^{(-a)}$  and  $\text{CO}_3^{(-2a)}$ . The concentration of  $\text{HCO}_3^{(-a)}$  is highest, being at  $k > 1.4$  about 0.06. In the process of  $\text{CO}_2^{(g)}$  binding also the pH value of the pulp changes. This phenomenon is discussed below.

So, in the contact of the air with ash pulp, about 1.15 moles of  $\text{CO}_2^{(g)}$  can be bound by 1 mole of free CaO in the pulp or 4.3 moles of  $\text{CO}_2^{(g)}$  by 1 kg oil shale. Certainly, due to the low concentration of  $\text{CO}_2^{(g)}$  in the air, huge quantities of the air must be used.

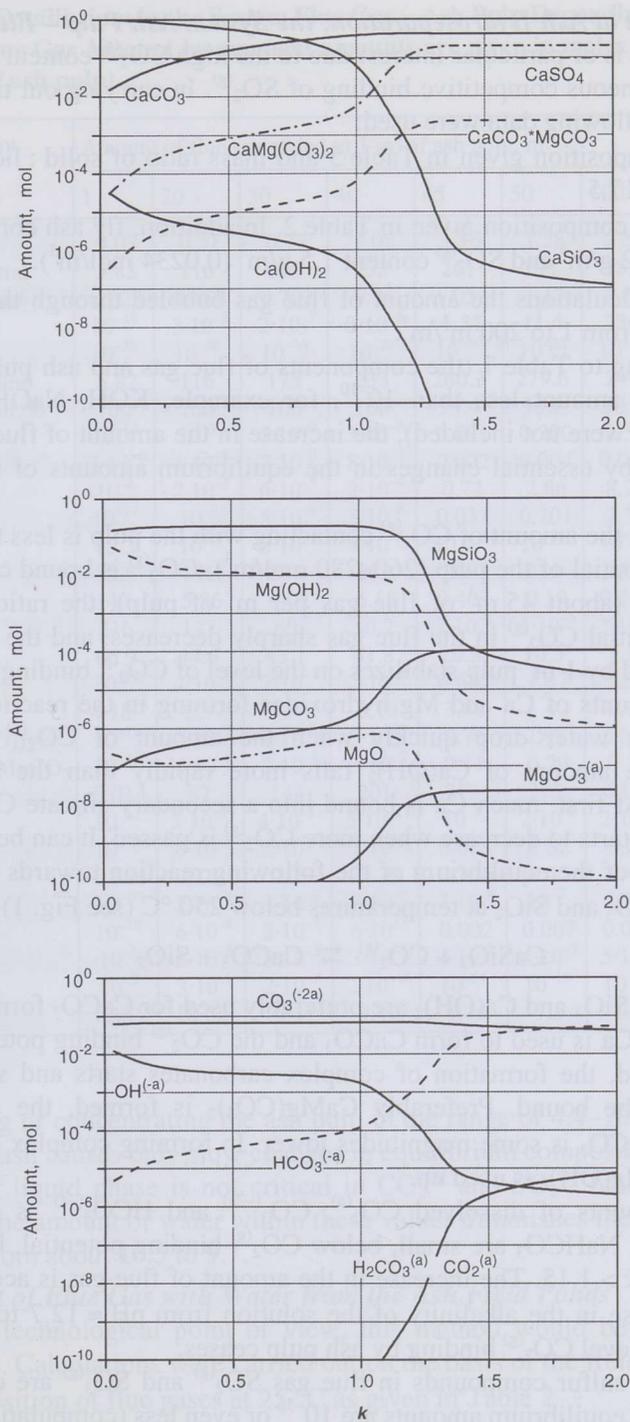


Fig. 5. Equilibrium amounts of components in the system of air – ash pulp depending on factor  $k$ : a – Ca compounds; b – Mg compounds; c –  $\text{CO}_2^{(g)}$  derivatives

### Equilibrium at Ash Hydroseparation; the System Ash Pulp – Flue Gas

This system is of particular interest due to the high  $\text{CO}_2^{(g)}$  content of flue gas and simultaneous competitive binding of  $\text{SO}_2^{(g)}$ . In carrying out the calculations, the following data were used:

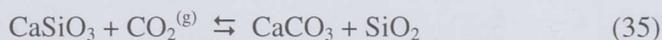
- Ash composition given in Table 5 and mass ratio of solid : liquid in the pulp 1 : 17.5
- Flue gas composition given in Table 2. In addition, fly ash content of the flue gas  $2 \text{ g/m}^3$  and  $\text{SO}_2^{(g)}$  content  $1.5 \text{ g/m}^3$  ( $0.0234 \text{ mol/m}^3$ ).

In the calculations the amount of flue gas bubbled through the ash pulp was varied from 1 to  $200 \text{ m}^3/\text{m}^3$ .

According to Table 7 (the components of flue gas and ash pulp with the equilibrium amount less than  $10^{-10}$ , for example, KOH, NaOH,  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$  etc. were not included), the increase in the amount of flue gas is accompanied by essential changes in the equilibrium amounts of the system components.

As far as the amount of  $\text{CO}_2^{(g)}$  contacting with the pulp is less than  $\text{CO}_2^{(g)}$  binding potential of the pulp ( $260\text{--}280 \text{ mol/m}^3$ ),  $\text{CO}_2^{(g)}$  is bound completely. At  $k > 1.15$  (about  $45 \text{ m}^3$  of flue gas per  $\text{m}^3$  of pulp), the ratio of  $\text{CO}_2^{(g)}$  bound to initial  $\text{CO}_2^{(g)}$  in the flue gas sharply decreases, and the amount of  $\text{CO}_2^{(g)}$  bound by  $1 \text{ m}^3$  pulp stabilizes on the level of  $\text{CO}_2^{(g)}$  binding potential.

The amounts of Ca and Mg hydroxides forming in the reaction of their oxides with water drop quickly when the amount of  $\text{CO}_2^{(g)}$  increases, whereas the amount of  $\text{Ca}(\text{OH})_2$  falls more rapidly than the amount of  $\text{Mg}(\text{OH})_2$ . At first, much Ca is bound into a secondary silicate  $\text{CaSiO}_3$ , but its amount starts to decrease when more  $\text{CO}_2^{(g)}$  is passed. It can be explained by the shift of the equilibrium of the following reaction towards the formation of  $\text{CaCO}_3$  and  $\text{SiO}_2$  at temperatures below  $250 \text{ }^\circ\text{C}$  (see Fig. 1):



Thus,  $\text{CaSiO}_3$  and  $\text{Ca}(\text{OH})_2$  are preferably used for  $\text{CaCO}_3$  formation. After most of Ca is used to form  $\text{CaCO}_3$  and the  $\text{CO}_2^{(g)}$  binding potential is almost utilized, the formation of complex carbonates starts and some more  $\text{CO}_2^{(g)}$  can be bound. Preferably  $\text{CaMg}(\text{CO}_3)_2$  is formed, the amount of  $\text{CaCO}_3 \cdot \text{MgCO}_3$  is some magnitudes lower. In forming complex carbonates almost all  $\text{Mg}(\text{OH})_2$  is used up.

The amounts of dissolved  $\text{CO}_2^{(a)}$ ,  $\text{CO}_3^{(-2a)}$  and  $\text{HCO}_3^{(-a)}$  as well as of  $\text{KHCO}_3$  and  $\text{NaHCO}_3$  are small, below  $\text{CO}_2^{(g)}$  binding potential, but start to increase at  $k > 1.15$ . The increase in the amount of flue gas is accompanied by a decrease in the alkalinity of the solution from  $\text{pH} \approx 12.7$  to  $\text{pH} \approx 8.5$ . On this pH level  $\text{CO}_2^{(g)}$  binding by ash pulp ceases.

Gaseous sulfur compounds in flue gas  $\text{SO}_2^{(g)}$  and  $\text{SO}_3^{(g)}$  are completely bound, their equilibrium amounts are  $10^{-36}$  or even less (computational limits of HSC [8]). Binding products are  $\text{CaSO}_4$  and  $\text{Na}_2\text{SO}_4$ , the amounts of other sulfates are negligible.

**Table 7. Equilibrium in the System Flue Gas – Ash Pulp Depending on the Flue Gas Amount (component amounts are given in moles per m<sup>3</sup> of ash pulp)**

Component or parameter	Amount of flue gas added to 1 m <sup>3</sup> of ash pulp, m <sup>3</sup>							
	1	20	30	40	45	50	100	200
<i>k</i>	0.03	0.51	0.77	1.02	1.15	1.28	2.56	5.1
CO <sub>2</sub> <sup>(g)</sup> initial	5.82	116	175	233	261	291	582	1164
SO <sub>2</sub> <sup>(g)</sup> initial	0.023	0.468	0.702	0.94	1.053	1.17	2.34	4.68
CO <sub>2</sub> <sup>(g)</sup>	10 <sup>-14</sup>	3·10 <sup>-8</sup>	2·10 <sup>-7</sup>	3·10 <sup>-6</sup>	1.57	11.4	286	867
SO <sub>2</sub> <sup>(g)</sup>	10 <sup>-36</sup>	10 <sup>-36</sup>	10 <sup>-36</sup>	10 <sup>-36</sup>	10 <sup>-36</sup>	10 <sup>-36</sup>	10 <sup>-36</sup>	10 <sup>-36</sup>
CO <sub>2</sub> <sup>(g)</sup> bound	5.82	116	175	233	260.3	279.6	296	297
CO <sub>2</sub> bound, %	100	100	100	100	99.4	96.1	50.9	25.3
CO <sub>2</sub> <sup>(a)</sup>	10 <sup>-14</sup>	10 <sup>-9</sup>	5·10 <sup>-9</sup>	3·10 <sup>-6</sup>	0.031	0.200	2.35	3.43
CO <sub>3</sub> <sup>(-2a)</sup>	2·10 <sup>-6</sup>	4·10 <sup>-5</sup>	7·10 <sup>-5</sup>	8·10 <sup>-3</sup>	0.002	0.004	0.003	0.002
HCO <sub>3</sub> <sup>(-a)</sup>	10 <sup>-8</sup>	2·10 <sup>-5</sup>	6·10 <sup>-5</sup>	2·10 <sup>-4</sup>	0.72	2.86	8.29	8.81
H <sub>2</sub> CO <sub>3</sub> <sup>(a)</sup>	10 <sup>-14</sup>	10 <sup>-9</sup>	5·10 <sup>-9</sup>	3·10 <sup>-6</sup>	0.031	0.201	2.36	3.45
Ca(OH) <sub>2</sub>	12.3	10 <sup>-3</sup>	3·10 <sup>-4</sup>	4·10 <sup>-5</sup>	8·10 <sup>-11</sup>	10 <sup>-11</sup>	10 <sup>-12</sup>	10 <sup>-13</sup>
CaCO <sub>3</sub>	35.5	146	204	263	269	254	248	251
CaSO <sub>4</sub>	14.6	5.86	6.02	6.18	0.403	0.19	0.247	0.356
CaSiO <sub>3</sub>	216	127	69	10.2	2·10 <sup>-5</sup>	3·10 <sup>-6</sup>	3·10 <sup>-7</sup>	2·10 <sup>-7</sup>
Mg(OH) <sub>2</sub>	46.9	44.6	43.1	41.8	26.5	10.5	1.11	0.71
MgCO <sub>3</sub>	10 <sup>-12</sup>	4·10 <sup>-8</sup>	2·10 <sup>-7</sup>	2·10 <sup>-6</sup>	0.687	1.87	2.38	2.22
MgSiO <sub>3</sub>	4·10 <sup>-4</sup>	2.39	3.84	5.19	3.48	1.40	0.15	0.095
CaMg(CO <sub>3</sub> ) <sub>2</sub>	10 <sup>-12</sup>	3·10 <sup>-7</sup>	2·10 <sup>-6</sup>	3·10 <sup>-5</sup>	9.78	25.2	31.2	29.4
CaCO <sub>3</sub> · MgCO <sub>3</sub>	10 <sup>-14</sup>	4·10 <sup>-9</sup>	2·10 <sup>-8</sup>	3·10 <sup>-7</sup>	0.11	0.29	0.35	0.33
SiO <sub>2</sub>	0.014	87	144	201	213	215	217	217
K <sub>2</sub> CO <sub>3</sub>	10 <sup>-12</sup>	3·10 <sup>-11</sup>	4·10 <sup>-11</sup>	5·10 <sup>-11</sup>	10 <sup>-9</sup>	2·10 <sup>-9</sup>	2·10 <sup>-9</sup>	10 <sup>-9</sup>
KHCO <sub>3</sub>	10 <sup>-10</sup>	8·10 <sup>-8</sup>	2·10 <sup>-7</sup>	7·10 <sup>-7</sup>	0.003	0.02	0.03	0.04
K <sub>2</sub> SO <sub>4</sub>	0.134	0.29	0.29	0.29	0.396	0.42	0.46	0.50
Na <sub>2</sub> CO <sub>3</sub>	10 <sup>-10</sup>	2·10 <sup>-9</sup>	3·10 <sup>-9</sup>	3·10 <sup>-9</sup>	7·10 <sup>-8</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
NaHCO <sub>3</sub>	10 <sup>-10</sup>	6·10 <sup>-8</sup>	2·10 <sup>-7</sup>	6·10 <sup>-7</sup>	0.002	0.007	0.024	0.031
Na <sub>2</sub> SO <sub>4</sub>	10 <sup>-5</sup>	3·10 <sup>-5</sup>	3·10 <sup>-5</sup>	3·10 <sup>-5</sup>	4·10 <sup>-5</sup>	4·10 <sup>-5</sup>	5·10 <sup>-5</sup>	7·10 <sup>-5</sup>
Na <sub>2</sub> SiO <sub>3</sub>	10 <sup>-9</sup>	3·10 <sup>-9</sup>	2·10 <sup>-9</sup>	2·10 <sup>-10</sup>	10 <sup>-14</sup>	10 <sup>-15</sup>	10 <sup>-16</sup>	10 <sup>-16</sup>
pH	12.31	10.66	10.41	9.92	7.74	7.5	6.9	6.8

Diluting or concentrating the ash pulp in the range of 4.4–70 m<sup>3</sup> of water per ton of ash causes only slow changes in equilibrium compositions. So, the amount of liquid phase is not critical in CO<sub>2</sub><sup>(g)</sup> and SO<sub>2</sub><sup>(g)</sup> binding. An increase in the amount of water within these values diminishes the pH value of the pulp from about 10.5 to 9.7.

#### **Treatment of Flue Gas with Water from the Ash Field Ponds**

From the technological point of view, this method would be most easily applicable. Calculations were carried out on the basis of the following data:

- Composition of flue gases at 25 °C as given in Table 2
- Mean composition of the water from the ponds of ash fields, calculated from [9] in moles per m<sup>3</sup> of water

	Pond No. 1 – working pond	Pond No. 2 – pond in reserve
Na <sup>(+a)</sup>	6.52	7.61
K <sup>(+a)</sup>	107.1	50.78
Ca <sup>(+2a)</sup>	16.14	0.35
SO <sub>4</sub> <sup>(-2a)</sup>	20.1	8.20
CO <sub>3</sub> <sup>(-2a)</sup>	4.5	14.23
OH <sup>(-a)</sup>	71.5	11.06
Cl <sup>(-a)</sup>	25.2	–
HCO <sub>3</sub> <sup>(-a)</sup>	–	3.17

The amounts of flue gas were varied within 0.5 to 30 m<sup>3</sup> per m<sup>3</sup> of water and, compared to the amounts used in previous calculations, they were significantly less due to the low binding potential of the liquid phase.

The amounts of CaCO<sub>3</sub> and MgCO<sub>3</sub> increase together with the amount of CO<sub>2</sub><sup>(g)</sup> bound, however, the amount of MgCO<sub>3</sub> is 2 to 4 magnitudes less. Noticeable formation of complex carbonates starts around the CO<sub>2</sub><sup>(g)</sup> binding limits – at about 7 or 1 m<sup>3</sup>/m<sup>3</sup> in the case of a working pond and a pond in reserve, respectively. Formation of CaMg(CO<sub>3</sub>)<sub>2</sub> is preferred, the amount of CaCO<sub>3</sub> · MgCO<sub>3</sub> is almost two magnitudes less. The amount of dissolved CO<sub>2</sub><sup>(a)</sup> is low until the binding potential is not achieved, above the limit it starts to grow, stabilizes on the level of about 0.6 mol/m<sup>3</sup> and reaches 3 mol/m<sup>3</sup> in a great excess of CO<sub>2</sub><sup>(g)</sup>.

The amounts of NaHCO<sub>3</sub> and KHCO<sub>3</sub> in the liquid phase increase together with the amount of flue gas, formation of their carbonates is of low importance – the amounts of carbonates do not exceed 10<sup>-5</sup> mol/m<sup>3</sup>. The increase in the amount of CO<sub>2</sub><sup>(g)</sup> bound results in the drop of solution alkalinity to pH = 8.2 at which the CO<sub>2</sub><sup>(g)</sup> binding potential is utilized. If the binding potential of a working pond is about 60 moles of CO<sub>2</sub><sup>(g)</sup> per m<sup>3</sup> of water, then in the case of a reserve pond this value is only 24 mol/m<sup>3</sup>. Gaseous sulfur compounds are bound completely; their equilibrium amounts are less than 10<sup>-36</sup> mol/m<sup>3</sup>.

### ***Effect of Liquid Phase pH on CO<sub>2</sub> Binding***

In the case of all the processes where CO<sub>2</sub><sup>(g)</sup> (from air or flue gas) is in contact with reaction products in the liquid phase, the following general regularities can be drawn:

- CO<sub>2</sub><sup>(g)</sup> binding ability depends only on the amount of active components (especially, on the initial amount of Ca and Mg hydroxides) in the liquid phase, not on the liquid : solid ratio.
- At high pH values (pH = 12–13), CO<sub>2</sub><sup>(g)</sup> is bound completely, whereas pH of the solution remains almost unchangeable. CO<sub>2</sub><sup>(g)</sup> is bound mainly as CaCO<sub>3</sub>, the formation of other carbonates is of less importance.

- At pH = 10–11 the contacted  $\text{CO}_2^{(g)}$  is bound completely. pH value of the solution does not characterize the overall  $\text{CO}_2^{(g)}$  binding capacity of the solution. The main product is  $\text{CaCO}_3$ .
- At pH  $\approx$  9 a decrease in the ratio of  $\text{CO}_2^{(g)}$  bound to contacted  $\text{CO}_2^{(g)}$  can be followed.  $\text{CO}_2^{(g)}$  binding capacity is utilized to the extent of 90–95 %. The formation of  $\text{CaMg}(\text{CO}_3)_2$  as well as of carbonic acid and its ions starts, which can be followed by the increase in the amounts of  $\text{NaHCO}_3$  and  $\text{KHCO}_3$ .
- At pH  $\approx$  8 the ratio of  $\text{CO}_2^{(g)}$  bound to contacted  $\text{CO}_2^{(g)}$  drops sharply, the binding capacity is utilized to the extent of over 98 %.  $\text{CaCO}_3\text{-MgCO}_3$  appears in the products, however, as compared to the amounts of  $\text{CaMg}(\text{CO}_3)_2$  and  $\text{CaCO}_3$  its role in  $\text{CO}_2^{(g)}$  binding is of less importance. The increase in  $\text{CO}_2^{(g)}$  binding is mainly due to the increase in the amount of dissolved  $\text{CO}_2^{(a)}$  and  $\text{HCO}_3^{(-a)}$ .
- At pH  $\approx$  7.5 the  $\text{CO}_2^{(g)}$  binding capacity (calculated from the initial content of free CaO and MgO) is completely utilized. Further binding is only due to the slow increase in the amount of dissolved  $\text{CO}_2^{(a)}$ .

## Conclusions

1. On the basis of calculated temperature dependencies of Gibbs free energy changes it was shown that oil shale ash is capable to bind simultaneously both carbon dioxide and sulfur dioxide in the system of flue gas – fly ash. A more deep decline in the equilibrium concentration of sulfur dioxide indicates its higher reaction ability, so,  $\text{SO}_2^{(g)}$  is bound preferably.
2. If equilibrium is reached, the  $\text{CO}_2^{(g)}$ -binding capacity of oil shale ash both in the system of flue gas – fly ash (gas – solid) and flue gas – ash pulp (liquid – solid – gas) is completely utilized.
3. Regularities in the changes in the pH value of ash pulp and water from the ash field ponds during their contact with flue gas were established. The main product formed during  $\text{CO}_2^{(g)}$  binding is  $\text{CaCO}_3$ , the role of other carbonates is of lesser importance. At pH values 9–10,  $\text{CO}_2^{(g)}$  binding from flue gas is complete. Decrease in pH to 8–9 indicates that the  $\text{CO}_2^{(g)}$  binding potential of the pulp or water is almost utilised.
4. Since due to the reactions between fly ash components and flue gas the amount of  $\text{CO}_2^{(g)}$  in the flue gas drops significantly in the temperature region of 300–200 °C, it should be reasonable to remove fly ash at these temperatures. The  $\text{CO}_2^{(g)}$  binding capacity of fly ash is on the level of 3.5 moles of  $\text{CO}_2^{(g)}$  per kg of oil shale, or 13.2 % of its total amount.
5. Essential reduction of  $\text{CO}_2$  content can be achieved by bubbling flue gas through the ash pulp formed at ash hydroseparation or through the water from the ash field ponds. The  $\text{CO}_2^{(g)}$  binding capacities of ash pulp and

of pond water are on the level of 260 moles and 60 or 30 (working pond or pond in reserve) moles of  $\text{CO}_2^{(g)}$  per  $\text{m}^3$  of liquid phase, respectively.

6. To improve the contact of liquid phase with the air during hydraulic ash removal to bind atmospheric  $\text{CO}_2^{(g)}$ , it is recommendable to aerate the water used in ash removal and to loosen the wet material in the ash fields mechanically.

## Acknowledgements

The financial support of Estonian Science Foundation (Grant No. 3662) is highly appreciated.

## REFERENCES

1. Global Warming. Hotting up in The Hauge // *The Economist*. 2000. No. 18. P. 101-104.
2. Kallaste, T., Liik, O., Ots, A. Possible energy sector trends in Estonia // *Context of Climate Change*. Tallinn, Vaba Maa, 1999 [in Estonian].
3. Kuusik, R., Kaljuvee, T., Veskimäe, H., Roundygin, Yu., Keltman, A. Reactivity of oil shale ashes toward sulfur dioxide. 3. Recurrent use of ash for flue gas purification // *Oil Shale*. 1999. Vol. 16, No. 4. P. 303-313.
4. Roundyguine, Y.A., Alfimov, G.V., Grigotyev, K.A., Roundyguine, A.Y., Kuusik, R., Kaljuvee, T. Use of oil shale waste ash for flue gas desulfurization // *Proc. 4th Intern. Symp. on Coal Combustion*, Beijing P.R. China, August 18-21, 1999 / Xu-Chang Xu, Hai-Ying Qui, Bao-Guo Fan (eds.). 1999. P. 171-176.
5. Kuusik, R., Kaljuvee, T. Types of oil shale ash and methods for increasing their reactivity // *Turning a Problem into a Resource: Remediation and Waste Management at the Sillamäe Site, Estonia* / C.R. Rofer, T. Kaasik (eds.). Dordrecht, Boston, London : Kluwer Academic Publishers, 2000. P. 215-222. ISBN 0-7923-6187-3 (Nato Science Series 1: Disarmament Technologies; Vol. 28).
6. Punning, J-M., Karindi, A. Composition of Estonian atmosphere // *Estonia in the System of Global Climate Change* / Institute of Ecology. Publications. 1996. Vol. 4. P. 26-34.
7. Kuusik, R., Veskimäe, H., Kaljuvee, T., Parts, O. Carbon dioxide binding in the heterogeneous systems formed by combustion of oil shale. 1. Carbon dioxide binding at oil shale ash deposits // *Oil Shale*. 2001. Vol. 18. No. 2. P. 109-122.
8. "Outokumpu JSC Chemistry® for Windows", version 4.0, Licence Ser. No. 40050 for Tallinn Technical University.
9. Oil shale minerals as valuable raw materials for building and chemical industry : Advertizing publication / Baltic Thermal Power Plant. - Narva, 1994 [in Estonian].

Presented by J. Kann

Received March 21, 2002