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

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SO_2 and CO_2 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_2 formed at oil shale combustion can be bound, and that SO_2 and SO_3 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_2 per m^3 of pulp. Dilution of the pulp does not affect the amount of CO_2 bound by the pulp. Water in the ponds of the ash fields can bind about 60–30 mol of CO_2 per m^3 of water, depending on whether the pond is in use or in reserve. In both cases the binding of SO_2 is favourable compared to the binding of CO_2.

Introduction

The main environmentally hazardous components in the flue gases formed at oil shale combustion are sulfur dioxide SO_2 and carbon dioxide CO_2. 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_2 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_2 emission is quite relevant in Estonia where the annual amount of CO_2 released is 13.5 tons per capita [2]. The main source of CO_2 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_2 binding by the ash is an actual process – in the power stations working on oil shale about 75–80 % of SO_2 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_2 by oil shale ash is quite a new topic [6, 7].

To elucidate the possibilities for reducing CO_2 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 ΔG_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 ΔG_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)
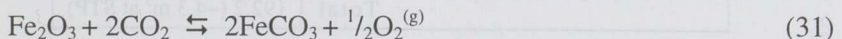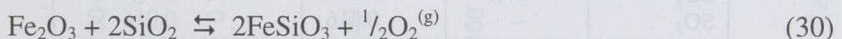
Results and Discussion

System Flue Gas – Fly Ash

Probable Reactions and Initial Composition of the Phases
In the first approach, temperature dependencies of Gibbs free energy changes ΔG_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 ($CO_2^{(a)}$ – 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

$$CaO + CO_2^{(g)} \leftrightarrows CaCO_3 \tag{1}$$

$$CaO + SO_2^{(g)} \leftrightarrows CaSO_3 \tag{2}$$

$$CaO + SO_2^{(g)} + {}^1/_2O_2^{(g)} \leftrightarrows CaSO_4 \tag{3}$$

$$SO_2 + {}^1/_2O_2^{(g)} \leftrightarrows SO_3^{(g)} \tag{4}$$

$$CaO + SO_3^{(g)} \leftrightarrows CaSO_4 \tag{5}$$

$$MgO + CO_2^{(g)} \leftrightarrows MgCO_3 \tag{6}$$

$$MgO + SO_2^{(g)} \leftrightarrows MgSO_3 \tag{7}$$

$$MgO + SO_2^{(g)} + {}^1/_2O_2^{(g)} \leftrightarrows MgSO_4 \tag{8}$$

$$MgO + SO_3^{(g)} \leftrightarrows MgSO_4 \tag{9}$$

$$Fe_2O_3 + 3SO_3^{(g)} \leftrightarrows Fe_2(SO_4)_3 \tag{10}$$

$$Al_2O_3 + 3SO_3^{(g)} \leftrightarrows Al_2(SO_4)_3 \tag{11}$$

$$K_2O + CO_2^{(g)} \leftrightarrows K_2CO_3 \tag{12}$$

$$Na_2O + CO_2^{(g)} \leftrightarrows Na_2CO_3 \tag{13}$$

$$K_2O + SO_2^{(g)} \leftrightarrows K_2SO_3 \tag{14}$$

$$Na_2O + SO_2^{(g)} \leftrightarrows Na_2SO_3 \tag{15}$$

$$K_2O + SO_3^{(g)} \leftrightarrows K_2SO_4 \tag{16}$$

$$Na_2O + SO_3^{(g)} \leftrightarrows Na_2SO_4 \tag{17}$$

$$Na_2O + H_2O + 2CO_2^{(g)} \leftrightarrows 2NaHCO_3 \tag{18}$$

$$K_2O + H_2O + 2CO_2^{(g)} \leftrightarrows 2KHCO_3 \tag{19}$$

$$Na_2O + SiO_2 \leftrightarrows Na_2SiO_3 \tag{20}$$

$$CaO + MgO + 2CO_2^{(g)} \leftrightarrows CaMg(CO_3)_2 \tag{21}$$

$$CaO + SiO_2 \leftrightarrows CaSiO_3 \tag{22}$$

$$MgO + SiO_2 \leftrightarrows MgSiO_3 \tag{23}$$

$$CaO + MgO \leftrightarrows CaO \cdot MgO \tag{24}$$

$$CaO + MgO + 2CO_2^{(g)} \leftrightarrows CaCO_3 \cdot MgCO_3 \tag{25}$$

$$CaO + H_2O^{(g)} \leftrightarrows Ca(OH)_2 \tag{26}$$

$$MgO + H_2O^{(g)} \leftrightarrows Mg(OH)_2 \tag{27}$$

$$Fe_2O_3 + 3H_2O^{(g)} \leftrightarrows 2Fe(OH)_3 \tag{28}$$

$$Al_2O_3 + 3H_2O^{(g)} \leftrightarrows 2Al(OH)_3 \tag{29}$$

$$Fe_2O_3 + 2SiO_2 \leftrightarrows 2FeSiO_3 + {}^1/_2O_2^{(g)} \tag{30}$$

$$Fe_2O_3 + 2CO_2 \leftrightarrows 2FeCO_3 + {}^1/_2O_2^{(g)} \tag{31}$$

$$FeS_2 + 2^3/_4 O_2^{(g)} \leftrightarrows {}^1/_2 Fe_2O_3 + 2SO_2^{(g)} \tag{32}$$

$$CaCO_3 + SO_2^{(g)} + {}^1/_2 O_2^{(g)} \leftrightarrows CaSO_4 + CO_2^{(g)} \tag{33}$$

$$CaMg(CO_3)_2 + 2SO_2^{(g)} + O_2^{(g)} \leftrightarrows CaSO_4 + MgSO_4 + 2CO_2^{(g)} \tag{34}$$

The temperature dependencies of ΔG_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, $CO_2^{(g)}$ from carbonates (46 % of the mass of carbonaceous fraction [2]) and FeS_2 from the clayey part of the mineral matter (12.3 % of the mass of clay fraction) which burns to give Fe_2O_3 and $SO_2^{(g)}$ 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
SiO₂	33.70	153.9	2.56
MgO	1.99	9.1	0.23
Al₂O₃	9.26	42.3	0.42
Fe₂O₃	4.73	21.6	0.14
FeO	0.16	0.8	0.01
K₂O	3.57	16.3	0.17
Na₂O	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 λ = 1.2)**

Component	From organic part	From mineral part	Total
CO₂	22.59	3.92	26.51
H₂O	16.98	–	16.98
N₂	136.70	5.08	141.78
O₂	6.04	0.22	6.26
SO₂	0.19	0.54	0.72 (~10.7 g/m³)
SO₃	–	0.016	0.016
		Total	192.2 (~4.3 m³ at STP)

c

ΔG_T, kcal/mol

b

ΔG_T, kcal/mol

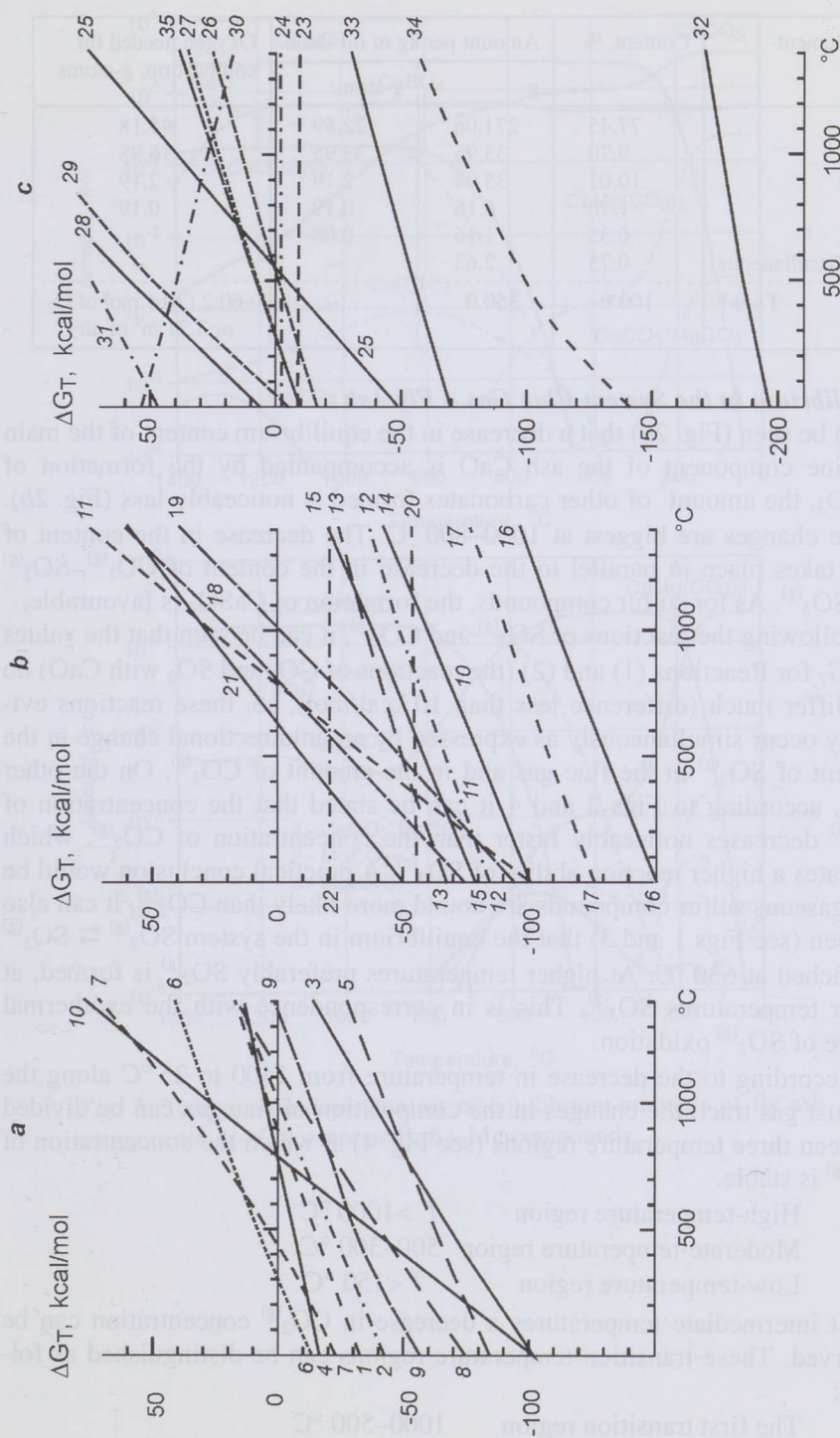a

ΔG_T, kcal/mol

°C

Fig. 1. Temperature dependences of Gibbs free energy changes ΔG_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_2 or 3.21 m^3 of air)

Equilibrium in the System Flue Gas – Fly Ash

It can be seen (Fig. 2*a*) that a decrease in the equilibrium content of the main alkaline component of the ash CaO is accompanied by the formation of $CaCO_3$, the amount* of other carbonates formed is noticeably less (Fig. 2*b*). 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 $CO_2^{(g)}$, $SO_2^{(g)}$ and $SO_3^{(g)}$. As for sulfur compounds, the formation of $CaSO_4$ is favourable.

Following the reactions of $SO_2^{(g)}$ and $CO_2^{(g)}$, it can be seen that the values of ΔG_T for Reactions (1) and (2) (the reactions of CO_2 and SO_2 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 $SO_2^{(g)}$ in the flue gas and in the amount of $CO_2^{(g)}$. On the other hand, according to Figs 3 and 4 it can be stated that the concentration of $SO_2^{(g)}$ decreases noticeably faster than the concentration of $CO_2^{(g)}$, which indicates a higher reaction ability of $SO_2^{(g)}$. A practical conclusion would be that gaseous sulfur compounds are bound more likely than $CO_2^{(g)}$. It can also be seen (see Figs 1 and 3) that the equilibrium in the system $SO_2^{(g)} \leftrightarrows SO_3^{(g)}$ is reached at 630 °C. At higher temperatures preferably $SO_2^{(g)}$ is formed, at lower temperatures $SO_3^{(g)}$. This is in correspondence with the exothermal nature of $SO_2^{(g)}$ 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 $CO_2^{(g)}$ 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 $CO_2^{(g)}$ 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

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* The amount in Table 4 and on Figs 2-4 is expressed in moles per kg of oil shale.
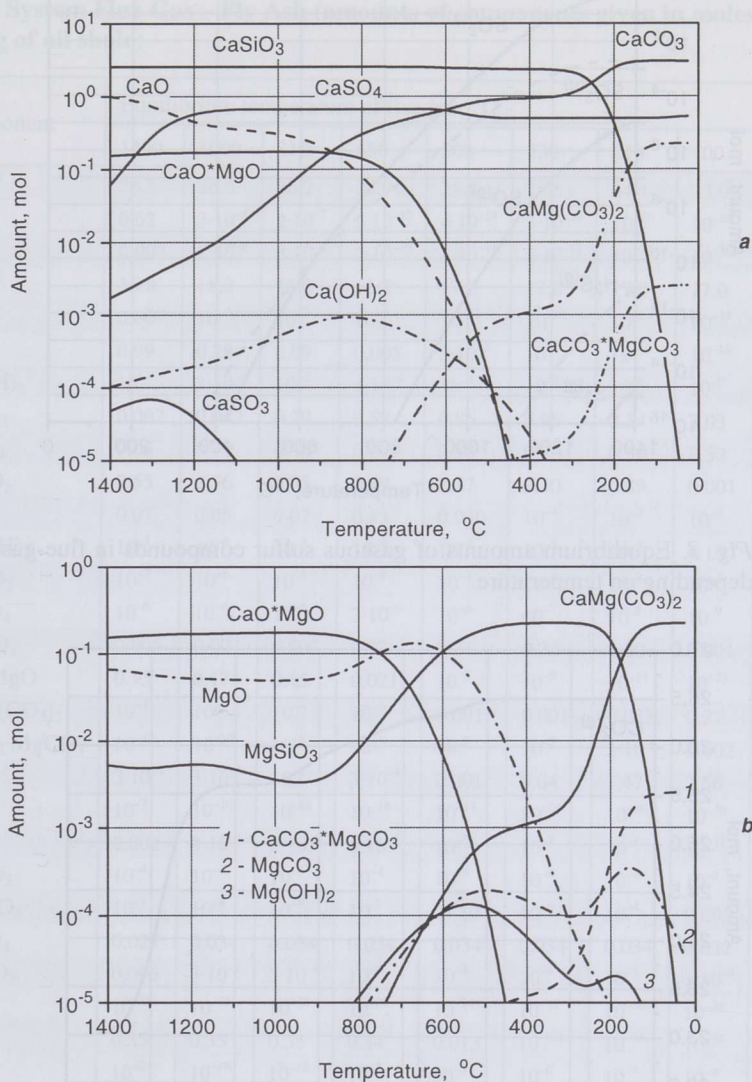
Fig. 2. Temperature dependencies of equilibrium amounts of fly ash components: *a* – Ca compounds; *b* – Mg compounds
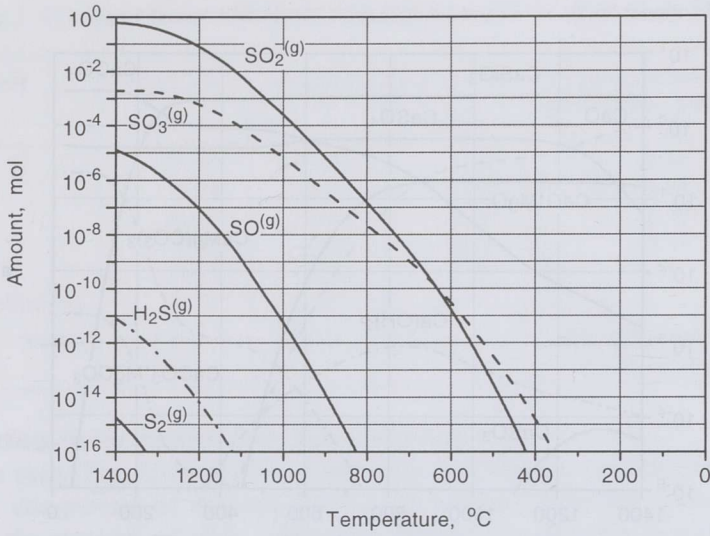
Fig. 3. Equilibrium amounts of gaseous sulfur compounds in flue gas depending on temperature
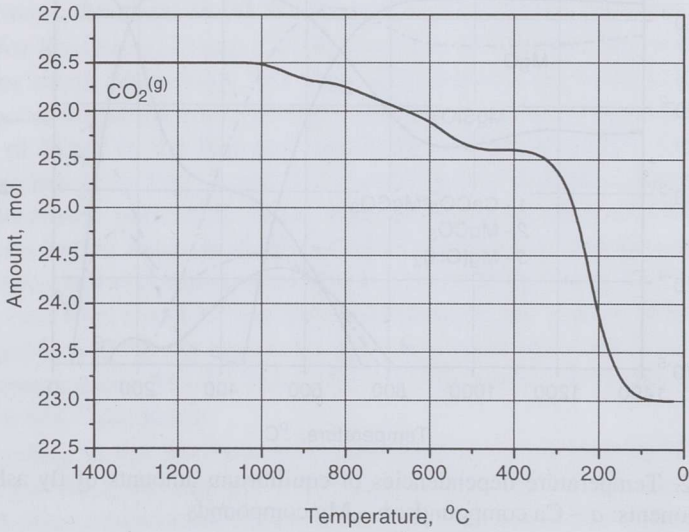

Fig. 4. Equilibrium amounts of carbon dioxide in flue gas depending on temperature

Table 4. **Temperature Dependence of the Equilibrium Composition of the System Flue Gas – Fly Ash (amounts of components given in moles per kg of oil shale)**

Component	Equilibrium temperature of flue gas, °C								
	1400	1000	810	650	500	330	210	100	25
$CO_2^{(g)}$	26.5	26.5	26.2	25.9	25.6	25.5	24.1	23.0	23.0
$SO_2^{(g)}$	0.62	$3 \cdot 10^{-4}$	$2 \cdot 10^{-7}$	$2 \cdot 10^{-10}$	$4 \cdot 10^{-14}$	$3 \cdot 10^{-20}$	10^{-27}	10^{-36}	10^{-36}
$SO_3^{(g)}$	0.002	$8 \cdot 10^{-6}$	$3 \cdot 10^{-8}$	$2 \cdot 10^{-10}$	$4 \cdot 10^{-13}$	$2 \cdot 10^{-17}$	10^{-22}	10^{-30}	10^{-36}
$H_2O^{(g)}$	16.8	16.8	16.8	16.8	17.0	17.0	17.0	17.0	5.58
$CO^{(g)}$	0.007	10^{-5}	10^{-7}	10^{-9}	10^{-12}	10^{-18}	10^{-24}	10^{-34}	10^{-36}
CaO	0.99	0.28	0.09	0.005	$5 \cdot 10^{-5}$	10^{-7}	10^{-10}	10^{-16}	10^{-22}
$Ca(OH)_2$	10^{-4}	$3 \cdot 10^{-4}$	10^{-3}	$4 \cdot 10^{-4}$	10^{-4}	10^{-5}	10^{-6}	10^{-9}	10^{-11}
$CaCO_3$	0.002	0.042	0.29	0.57	0.86	0.96	2.34	3.03	3.0
$CaSO_4$	0.06	0.71	0.66	0.67	0.50	0.50	0.50	0.50	0.53
$CaSiO_3$	2.55	2.56	2.55	2.49	2.37	2.30	0.89	0.001	10^{-6}
MgO	0.07	0.05	0.07	0.13	0.030	10^{-4}	10^{-5}	10^{-8}	10^{-12}
$Mg(OH)_2$	10^{-7}	10^{-6}	10^{-4}	10^{-4}	10^{-4}	10^{-5}	10^{-5}	$4 \cdot 10^{-6}$	10^{-7}
$MgCO_3$	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}
$MgSO_4$	10^{-6}	10^{-6}	10^{-6}	$3 \cdot 10^{-6}$	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-11}
$MgSiO_3$	0.005	0.004	0.007	0.07	0.21	0.22	0.20	0.001	10^{-6}
CaO·MgO	0.15	0.17	0.15	0.021	10^{-4}	10^{-9}	10^{-14}	10^{-23}	10^{-33}
$CaMg(CO_3)_2$	10^{-11}	10^{-8}	10^{-6}	10^{-4}	0.001	0.001	0.023	0.22	0.22
$CaCO_3·MgCO_3$	10^{-13}	10^{-10}	10^{-8}	10^{-6}	10^{-5}	10^{-5}	$3 \cdot 10^{-4}$	0.002	0.003
SiO_2	$3 \cdot 10^{-3}$	$3 \cdot 10^{-4}$	10^{-4}	$3 \cdot 10^{-4}$	0.001	0.04	1.47	2.56	2.56
Na_2O	10^{-7}	10^{-10}	10^{-12}	10^{-14}	10^{-17}	10^{-24}	10^{-30}	10^{-36}	10^{-36}
NaOH	0.002	$4 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$6 \cdot 10^{-5}$	10^{-5}	10^{-7}	10^{-8}	10^{-11}	10^{-15}
Na_2CO_3	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-5}	10^{-7}
$NaHCO_3$	10^{-9}	10^{-9}	10^{-8}	10^{-7}	$2 \cdot 10^{-7}$	10^{-6}	10^{-4}	0.005	0.06
Na_2SO_4	0.027	0.034	0.034	0.034	0.034	0.034	0.034	0.032	0.004
Na_2SiO_3	0.006	$3 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	10^{-4}	10^{-4}	10^{-4}	10^{-5}	$3 \cdot 10^{-9}$	10^{-13}
K_2O	10^{-28}	10^{-25}	10^{-23}	10^{-21}	10^{-24}	10^{-32}	10^{-36}	10^{-36}	10^{-36}
KOH	0.35	0.35	0.35	0.34	0.013	10^{-32}	10^{-36}	10^{-36}	10^{-36}
K_2CO_3	10^{-24}	10^{-16}	10^{-12}	10^{-7}	10^{-5}	10^{-6}	10^{-7}	10^{-9}	10^{-11}
$KHCO_3$	10^{-18}	10^{-14}	10^{-11}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	$3 \cdot 10^{-4}$	0.005
K_2SO_4	10^{-20}	10^{-13}	10^{-8}	10^{-3}	0.17	0.17	0.17	0.17	0.17
FeO	0.02	0.002	10^{-4}	10^{-5}	10^{-7}	10^{-9}	10^{-12}	10^{-17}	10^{-22}
Fe_2O_3	0.12	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
$Fe(OH)_3$	10^{-11}	10^{-11}	10^{-10}	10^{-10}	10^{-9}	10^{-9}	10^{-8}	10^{-7}	10^{-5}
$FeCO_3$	10^{-8}	$2 \cdot 10^{-9}$	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-16}	10^{-18}
$FeSiO_3$	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-8}	10^{-10}	10^{-15}	10^{-19}
Al_2O_3	0.42	0.42	0.42	0.42	0.42	0.42	0.42	042	0.39
$Al(OH)_3$	10^{-9}	10^{-9}	10^{-9}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-3}	0.06
FeS_2	10^{-24}	10^{-34}	10^{-36}	10^{-36}	10^{-36}	10^{-36}	10^{-36}	10^{-36}	10^{-36}

High-Temperature Region (T > 1000 °C)
In this temperature region the equilibrium amount of $CO_2^{(g)}$ 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 $CaSiO_3$ in the reaction
with SiO_2. Among Ca compounds, $CaSiO_3$ and CaO prevail. Amount of
$CaCO_3$ is low, but increases from 10^{-3} to 0.1 mol/kg with decreasing tem-
perature. Much calcium is utilized in binding gaseous sulfur compounds; the
main product formed is $CaSO_4$. Part of MgO reacts with SiO_2 to give
$MgSiO_3$, and another part with CaO to give $CaO \cdot MgO$. The amount of
$MgCO_3$ is low. SiO_2 is completely utilized in forming secondary Ca and Mg
silicates.
    At higher temperatures of this region, the amount of $SO_2^{(g)}$ formed is rela-
tively high – 0.62 mol/kg (concentration in the flue gas ~9 g/m^3). At tem-
peratures near 1000 °C it decreases to $3 \cdot 10^{-4}$ mol/kg (concentration
~6 mg/m^3). The amount of $SO_3^{(g)}$ is some magnitudes lower. So, in this tem-
perature 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 $CO_2^{(g)}$ amount from 26.5
to 25.6 mol/kg (see Fig. 4), accompanied by a decrease in the amount of
CaO·MgO and an increase in the amount of $CaCO_3$. 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 $MgSiO_3$ increases and reaches its maximum level (see Fig. 2*b*).
The amount of $CaSiO_3$ remains practically unchangeable. The amount of
$CaSO_4$ falls to its final level.
    The amount of free $SO_2^{(g)}$ drops to $4 \cdot 10^{-14}$ mol/kg (~6 mg/m^3), the
amount of free $SO_3^{(g)}$ is on the same level (see Fig. 3).

Moderate Temperature Region (500–300 °C)
The amount of $CO_2^{(g)}$ is steady (25.6–25.5 mol/kg). The formation of
$CaMg(CO_3)_2$ continues and, therefore, the amount of free MgO decreases by
even more than three magnitudes.
    The amount of $CaSiO_3$ 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 K_2SO_4 increases and of other sulfates decreases. The amount of
K_2SO_4 reaches its maximum level, whilst the amount of Na_2SO_4 drops.

The Second Transition Region (300–150 °C)
A considerable decrease in $CO_2^{(g)}$ amount from 25.5 to almost the final level
23.1 mol/kg takes place. It is due to a more intensive formation of $CaCO_3$
accompanied by a decrease in the amount of CaO, $CaO \cdot MgO$ and, espe-
cially, 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 $CaMg(CO_3)_2$, starts, but its amount is still one-two magnitudes less than that of $CaCO_3$. Besides, some $CaCO_3 \cdot MgCO_3$ is formed.

The formation of $KHCO_3$ and $NaHCO_3$ starts, but their amount is still negligible, the amounts of K_2SO_4 and Na_2SO_4 remain unchangeable.

Low-Temperature Region (150–25 °C)

At temperatures below 150 °C, the amount of $CO_2^{(g)}$ 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 SiO_2. At temperatures below 100 °C water vapour begins to condense and processes characteristic to ash hydroseparation could start.

The binding of $CO_2^{(g)}$ can occur up to room temperature. All together, $26.5 - 23.0 = 3.5$ moles of $CO_2^{(g)}$ per kg of oil shale is bound, or the 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 $SO_2^{(g)}$ and $SO_3^{(g)}$ formed at oil shale combustion should be completely bound when the flue gas temperature decreases to 450 °C. The main products are $CaSO_4$, K_2SO_4 and Na_2SO_4 which bind about 0.57, 0.17 and 0.004 moles of $SO_x^{(g)}$ per kg of oil shale, respectively (the initial amount being 0.74 mol/kg). The amount of $MgSO_4$ 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: $Ca^{(+2a)}$, $Mg^{(+2a)}$, $Na^{(+a)}$, $K^{(+a)}$, $H_2CO_3^{(a)}$, $HCO_3^{(-a)}$, $CO_2^{(-2a)}$, $OH^{(-a)}$ take part in the reactions
- The components of the air $N_2^{(g)}$, $O_2^{(g)}$, $CO_2^{(g)}$, $CO^{(g)}$ are considered in the calculations

In the calculations a factor k (Table 6) was used to describe the mole ratio of $CO_2^{(g)}$ contacted with the pulp and free CaO present in the initial pulp.

According to Table 6, all the $CO_2^{(g)}$ is bound up to the value of $k = 1.05$, further on the degree of $CO_2^{(g)}$ binding decreases and $CO_2^{(g)}$ content of the gas phase increases. When k approaches $k \approx 1$ (Fig. 5a,b), the formation of complex carbonate $CaMg(CO_3)_2$ starts in addition to the formation of $CaCO_3$. At $k \approx 1.1$ Mg is completely bound as $CaMg(CO_3)_2$. Saturation of the pulp with $CO_2^{(g)}$ is achieved on the level of $k \approx 1.15$, at that 90 % of calcium is bound into $CaCO_3$ and 10 % occurs as $CaMg(CO_3)_2$.

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

Component	Content	
	%	moles per m³ of pulp
CaO	23.6	227.5
SiO₂	24.0	275.9
Al₂O₃	7.0	37.11
Fe₂O₃	5.0	16.93
MgO	2.0	46.94
K₂O	2.0	15.64
Na₂O	0.1	0.87
CaSO₄	5.5	21.84
CaCO₃	5.5	29.70
Miscellaneous	23.83	–

Table 6. **Dependence of $CO_2^{(g)}$ Binding on $CO_2^{(g)}$ Added**

k	0.035	0.5	0.9	1.05	1.15	1.45	2.1	3.1
$CO_2^{(g)}$ in gas phase[1]	10⁻¹²	3·10⁻⁷	10⁻⁶	3·10⁻⁶	0.015	0.3	0.95	1.94
$CO_2^{(g)}$ bound[2]	0.035	0.5	0.9	1.05	1.135	1.15	1.15	1.16
$CO_2^{(g)}$ bound, %[3]	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 $CO_2^{(g)}$ bound by pulp.
[3] – amount of $CO_2^{(g)}$ bound in percent from total.

Additional binding of $CO_2^{(g)}$ is achieved due to its dissolution in aqueous phase of the pulp (Fig. 5c) with the formation of H_2CO_3 and its dissociation products $HCO_3^{(-a)}$ and $CO_3^{(-2a)}$. The concentration of $HCO_3^{(-a)}$ is highest, being at $k > 1.4$ about 0.06. In the process of $CO_2^{(g)}$ 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 $CO_2^{(g)}$ can be bound by 1 mole of free CaO in the pulp or 4.3 moles of $CO_2^{(g)}$ by 1 kg oil shale. Certainly, due to the low concentration of $CO_2^{(g)}$ in the air, huge quantities of the air must be used.

a

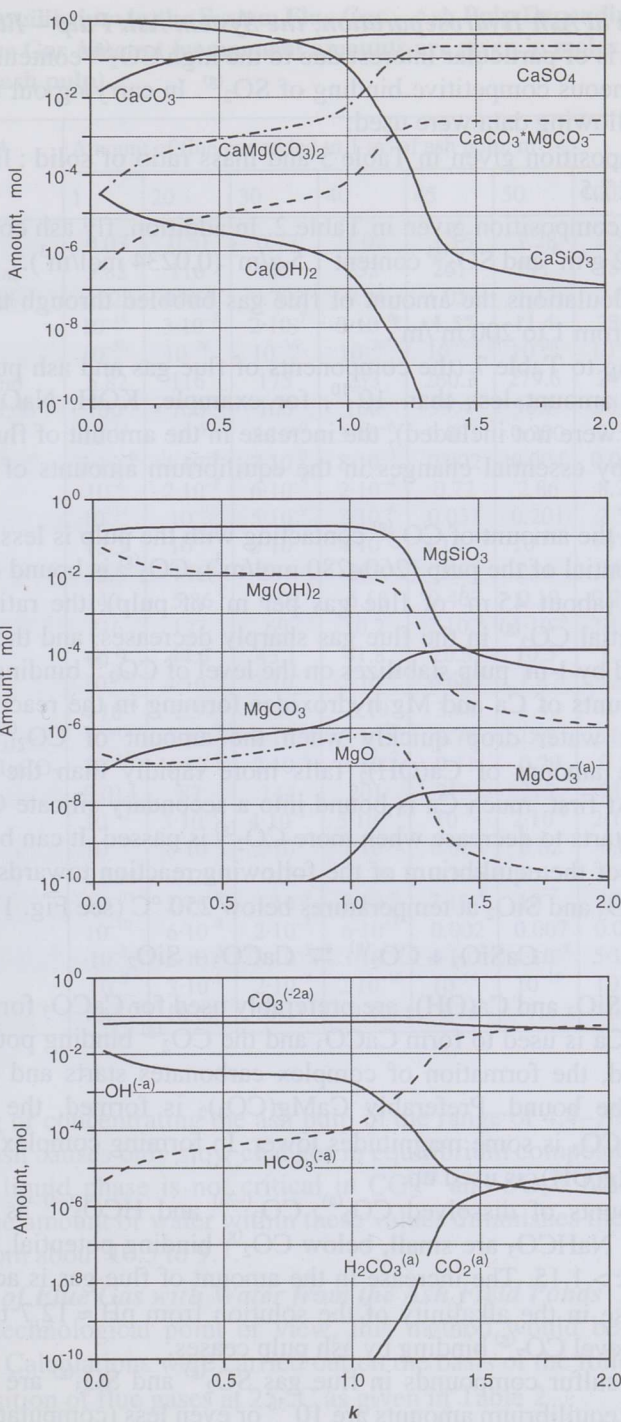Amount, mol

10^0 — 10^{-2} — 10^{-4} — 10^{-6} — 10^{-8} — 10^{-10}

0.0 — 0.5 — 1.0 — 1.5 — 2.0

$CaCO_3$ $CaSO_4$ $CaMg(CO_3)_2$ $CaCO_3 \cdot MgCO_3$ $Ca(OH)_2$ $CaSiO_3$

b

Amount, mol

10^0 — 10^{-2} — 10^{-4} — 10^{-6} — 10^{-8} — 10^{-10}

0.0 — 0.5 — 1.0 — 1.5 — 2.0

$MgSiO_3$ $Mg(OH)_2$ $MgCO_3$ MgO $MgCO_3^{-(a)}$

c

Amount, mol

10^0 — 10^{-2} — 10^{-4} — 10^{-6} — 10^{-8} — 10^{-10}

0.0 — 0.5 — 1.0 — 1.5 — 2.0

k

$CO_3^{(-2a)}$ $OH^{(-a)}$ $HCO_3^{(-a)}$ $H_2CO_3^{(a)}$ $CO_2^{(a)}$

Fig. 5. Equilibrium amounts of components in the system of air – ash pulp depending on factor k: a – Ca compounds; b – Mg compounds; c – $CO_2^{(g)}$ derivatives

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

This system is of particular interest due to the high $CO_2^{(g)}$ content of flue gas and simultaneous competitive binding of $SO_2^{(g)}$. 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 g/m^3 and $SO_2^{(g)}$ content 1.5 g/m^3 (0.0234 mol/m^3).

In the calculations the amount of flue gas bubbled through the ash pulp was varied from 1 to 200 m^3/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, $MgSO_4$, Na_2SO_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 $CO_2^{(g)}$ contacting with the pulp is less than $CO_2^{(g)}$ binding potential of the pulp (260–280 mol/m^3), $CO_2^{(g)}$ is bound completely. At $k > 1.15$ (about 45 m^3 of flue gas per m^3 of pulp), the ratio of $CO_2^{(g)}$ bound to initial $CO_2^{(g)}$ in the flue gas sharply decreases, and the amount of $CO_2^{(g)}$ bound by 1 m^3 pulp stabilizes on the level of $CO_2^{(g)}$ binding potential.

The amounts of Ca and Mg hydroxides forming in the reaction of their oxides with water drop quickly when the amount of $CO_2^{(g)}$ increases, whereas the amount of $Ca(OH)_2$ falls more rapidly than the amount of $Mg(OH)_2$. At first, much Ca is bound into a secondary silicate $CaSiO_3$, but its amount starts to decrease when more $CO_2^{(g)}$ is passed. It can be explained by the shift of the equilibrium of the following reaction towards the formation of $CaCO_3$ and SiO_2 at temperatures below 250 °C (see Fig. 1):

$$CaSiO_3 + CO_2^{(g)} \leftrightarrows CaCO_3 + SiO_2 \qquad (35)$$
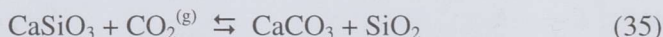
Thus, $CaSiO_3$ and $Ca(OH)_2$ are preferably used for $CaCO_3$ formation. After most of Ca is used to form $CaCO_3$ and the $CO_2^{(g)}$ binding potential is almost utilized, the formation of complex carbonates starts and some more $CO_2^{(g)}$ can be bound. Preferably $CaMg(CO_3)_2$ is formed, the amount of $CaCO_3 \cdot MgCO_3$ is some magnitudes lower. In forming complex carbonates almost all $Mg(OH)_2$ is used up.

The amounts of dissolved $CO_2^{(a)}$, $CO_3^{(-2a)}$ and $HCO_3^{(-a)}$ as well as of $KHCO_3$ and $NaHCO_3$ are small, below $CO_2^{(g)}$ 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 pH $\approx$ 12.7 to pH $\approx$ 8.5. On this pH level $CO_2^{(g)}$ binding by ash pulp ceases.

Gaseous sulfur compounds in flue gas $SO_2^{(g)}$ and $SO_3^{(g)}$ are completely bound, their equilibrium amounts are 10^{-36} or even less (computational limits of HSC [8]). Binding products are $CaSO_4$ and Na_2SO_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 m³ of ash pulp)**

Component or parameter	Amount of flue gas added to 1 m³ of ash pulp, m³							
	1	20	30	40	45	50	100	200
k	0.03	0.51	0.77	1.02	1.15	1.28	2.56	5.1
$CO_2^{(g)}$ initial	5.82	116	175	233	261	291	582	1164
$SO_2^{(g)}$ initial	0.023	0.468	0.702	0.94	1.053	1.17	2.34	4.68
$CO_2^{(g)}$	10^{-14}	$3·10^{-8}$	$2·10^{-7}$	$3·10^{-6}$	1.57	11.4	286	867
$SO_2^{(g)}$	10^{-36}	10^{-36}	10^{-36}	10^{-36}	10^{-36}	10^{-36}	10^{-36}	10^{-36}
$CO_2^{(g)}$ bound	5.82	116	175	233	260.3	279.6	296	297
CO_2 bound, %	100	100	100	100	99.4	96.1	50.9	25.3
$CO_2^{(a)}$	10^{-14}	10^{-9}	$5·10^{-9}$	$3·10^{-6}$	0.031	0.200	2.35	3.43
$CO_3^{(-2a)}$	$2·10^{-6}$	$4·10^{-5}$	$7·10^{-5}$	$8·10^{-3}$	0.002	0.004	0.003	0.002
$HCO_3^{(-a)}$	10^{-8}	$2·10^{-5}$	$6·10^{-5}$	$2·10^{-4}$	0.72	2.86	8.29	8.81
$H_2CO_3^{(a)}$	10^{-14}	10^{-9}	$5·10^{-9}$	$3·10^{-6}$	0.031	0.201	2.36	3.45
$Ca(OH)_2$	12.3	10^{-3}	$3·10^{-4}$	$4·10^{-5}$	$8·10^{-11}$	10^{-11}	10^{-12}	10^{-13}
$CaCO_3$	35.5	146	204	263	269	254	248	251
$CaSO_4$	14.6	5.86	6.02	6.18	0.403	0.19	0.247	0.356
$CaSiO_3$	216	127	69	10.2	$2·10^{-5}$	$3·10^{-6}$	$3·10^{-7}$	$2·10^{-7}$
$Mg(OH)_2$	46.9	44.6	43.1	41.8	26.5	10.5	1.11	0.71
$MgCO_3$	10^{-12}	$4·10^{-8}$	$2·10^{-7}$	$2·10^{-6}$	0.687	1.87	2.38	2.22
$MgSiO_3$	$4·10^{-4}$	2.39	3.84	5.19	3.48	1.40	0.15	0.095
$CaMg(CO_3)_2$	10^{-12}	$3·10^{-7}$	$2·10^{-6}$	$3·10^{-5}$	9.78	25.2	31.2	29.4
$CaCO_3·MgCO_3$	10^{-14}	$4·10^{-9}$	$2·10^{-8}$	$3·10^{-7}$	0.11	0.29	0.35	0.33
SiO_2	0.014	87	144	201	213	215	217	217
K_2CO_3	10^{-12}	$3·10^{-11}$	$4·10^{-11}$	$5·10^{-11}$	10^{-9}	$2·10^{-9}$	$2·10^{-9}$	10^{-9}
$KHCO_3$	10^{-10}	$8·10^{-8}$	$2·10^{-7}$	$7·10^{-7}$	0.003	0.02	0.03	0.04
K_2SO_4	0.134	0.29	0.29	0.29	0.396	0.42	0.46	0.50
Na_2CO_3	10^{-10}	$2·10^{-9}$	$3·10^{-9}$	$3·10^{-9}$	$7·10^{-8}$	10^{-7}	10^{-7}	10^{-7}
$NaHCO_3$	10^{-10}	$6·10^{-8}$	$2·10^{-7}$	$6·10^{-7}$	0.002	0.007	0.024	0.031
Na_2SO_4	10^{-5}	$3·10^{-5}$	$3·10^{-5}$	$3·10^{-5}$	$4·10^{-5}$	$4·10^{-5}$	$5·10^{-5}$	$7·10^{-5}$
Na_2SiO_3	10^{-9}	$3·10^{-9}$	$2·10^{-9}$	$2·10^{-10}$	10^{-14}	10^{-15}	10^{-16}	10^{-16}
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 m³ of water per ton of ash causes only slow changes in equilibrium compositions. So, the amount of liquid phase is not critical in $CO_2^{(g)}$ and $SO_2^{(g)}$ 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 m³ of water

	Pond No. 1 – working pond	Pond No. 2 – pond in reserve
$Na^{(+a)}$	6.52	7.61
$K^{(+a)}$	107.1	50.78
$Ca^{(+2a)}$	16.14	0.35
$SO_4^{(-2a)}$	20.1	8.20
$CO_3^{(-2a)}$	4.5	14.23
$OH^{(-a)}$	71.5	11.06
$Cl^{(-a)}$	25.2	–
$HCO_3^{(-a)}$	–	3.17

The amounts of flue gas were varied within 0.5 to 30 m^3 per m^3 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 $CaCO_3$ and $MgCO_3$ increase together with the amount of $CO_2^{(g)}$ bound, however, the amount of $MgCO_3$ is 2 to 4 magnitudes less. Noticeable formation of complex carbonates starts around the $CO_2^{(g)}$ binding limits – at about 7 or 1 m^3/m^3 in the case of a working pond and a pond in reserve, respectively. Formation of $CaMg(CO_3)_2$ is preferred, the amount of $CaCO_3 \cdot MgCO_3$ is almost two magnitudes less. The amount of dissolved $CO_2^{(a)}$ 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^3 and reaches 3 mol/m^3 in a great excess of $CO_2^{(g)}$.

The amounts of $NaHCO_3$ and $KHCO_3$ 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^{-5} mol/m^3. The increase in the amount of $CO_2^{(g)}$ bound results in the drop of solution alkalinity to pH = 8.2 at which the $CO_2^{(g)}$ binding potential is utilized. If the binding potential of a working pond is about 60 moles of $CO_2^{(g)}$ per m^3 of water, then in the case of a reserve pond this value is only 24 mol/m^3. Gaseous sulfur compounds are bound completely; their equilibrium amounts are less than 10^{-36} mol/m^3.

Effect of Liquid Phase pH on CO_2 Binding

In the case of all the processes where $CO_2^{(g)}$ (from air or flue gas) is in contact with reaction products in the liquid phase, the following general regularities can be drawn:

- $CO_2^{(g)}$ 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), $CO_2^{(g)}$ is bound completely, whereas pH of the solution remains almost unchangeable. $CO_2^{(g)}$ is bound mainly as $CaCO_3$, the formation of other carbonates is of less importance.

- At pH = 10–11 the contacted $CO_2^{(g)}$ is bound completely. pH value of the solution does not characterize the overall $CO_2^{(g)}$ binding capacity of the solution. The main product is $CaCO_3$.
- At pH ≈ 9 a decrease in the ratio of $CO_2^{(g)}$ bound to contacted $CO_2^{(g)}$ can be followed. $CO_2^{(g)}$ binding capacity is utilized to the extent of 90–95 %. The formation of $CaMg(CO_3)_2$ as well as of carbonic acid and its ions starts, which can be followed by the increase in the amounts of $NaHCO_3$ and $KHCO_3$.
- At pH ≈ 8 the ratio of $CO_2^{(g)}$ bound to contacted $CO_2^{(g)}$ drops sharply, the binding capacity is utilized to the extent of over 98 %. $CaCO_3 \cdot MgCO_3$ appears in the products, however, as compared to the amounts of $CaMg(CO_3)_2$ and $CaCO_3$ its role in $CO_2^{(g)}$ binding is of less importance. The increase in $CO_2^{(g)}$ binding is mainly due to the increase in the amount of dissolved $CO_2^{(a)}$ and $HCO_3^{(-a)}$.
- At pH ≈ 7.5 the $CO_2^{(g)}$ 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 $CO_2^{(a)}$.

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, $SO_2^{(g)}$ is bound preferably.
2. If equilibrium is reached, the $CO_2^{(g)}$-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 $CO_2^{(g)}$ binding is $CaCO_3$, the role of other carbonates is of lesser importance. At pH values 9–10, $CO_2^{(g)}$ binding from flue gas is complete. Decrease in pH to 8–9 indicates that the $CO_2^{(g)}$ 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 $CO_2^{(g)}$ 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 $CO_2^{(g)}$ binding capacity of fly ash is on the level of 3.5 moles of $CO_2^{(g)}$ per kg of oil shale, or 13.2 % of its total amount.
5. Essential reduction of 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 $CO_2^{(g)}$ 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 $CO_2^{(g)}$ per m^3 of liquid phase, respectively.

6. To improve the contact of liquid phase with the air during hydraulic ash removal to bind atmospheric $CO_2^{(g)}$, it is recommendable to aerate the water used in ash removal and to loosen the wet material in the ash fields mechanically.

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