ABATEMENT OF CO_2 EMISSION IN ESTONIAN ENERGY SECTOR

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Abstract

Energy production in the Republic of Estonia is based on the firing of local oil shale (about 10 mil. t per year), which is accompanied by high CO_2 emissions and formation of waste alkali ash in huge quantities. The water suspensions formed during hydraulic transport are strongly alkaline (pH 13.2 – 12.6) and therefore not suitable for releasing into the environment. To elucidate the possibilities for reducing CO_2 emissions and to find out regularities of CO_2 binding in the system of oil shale ash pulp - flue gases, thermodynamic analysis of the reactions occurring between the gaseous and solid combustion products formed from oil shale was carried out using the target-oriented HSC software. Laboratory scale experiments were conducted too. Suspensions formed during hydraulic transport of ash can bind up to 260 mol of CO_2 per m^3 of pulp. The experiments indicated that the ashes used bound actively CO_2 from flue gases. Under certain conditions, all the free CaO contained in the ash can be consumed with formation of $CaCO_3$ and thereby ash can be chemically stabilized. It means that on the production level of year 2000 the emission of CO_2 could be decreased in the amount of 700 000 t per year.

Introduction

Carbon dioxide formed at combustion of fossil fuels being 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^oC or by pessimistic assumptions even by 6^oC (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 based energetics. The carbon emission factor (CEF) of oil shale is 29.1 tC/TJ (2), of coal and natural gas 25.8 and 15.2 tC/TJ, respectively. The CEF for Estonian oil shale is higher due to its higher content of mineral CO_2 (carbonates) as compared to other fuels. The decomposition products of carbonates are free Ca, Mg-oxides; their content in ashes reaches up to 30% (3, 4). In certain conditions they could be the binders of acidic gases (SO_2, CO_2, etc.) (5, 6). It was assumed that the oil shale ash formed in huge amounts (42-48% of oil shale mass burned) could be carbonated by binding CO_2 from air during hydroseparation and deposition of it in wet dumps (in ash-fields) and decreasing by this the amount of CO_2 emitted, the respective amounts were estimated (7, 8, 9). Main task of our studies was the theoretical estimation of CO_2 binding processes as well as an experimental investigation of the process in the system ash water suspension – flue gases.

Methods

Thermodynamic analysis of the reactions occurring between the gaseous and solid products formed at oil shale combustion was carried out. Changes in Gibbs free energy ΔG_T, its temperature dependency and equilibrium composition of reaction products were calculated for a set of reactions using the HSC software (10). Model experiments were carried out using different kinds, but mainly cyclone ash formed at the Estonian Power Plant (town Narva, Estonia). The content of free CaO and CO_2 in the model ash (on dry bases) was 22.94% and 0.08%, respectively. Chemical composition of ash and flue gases is given in Tables 1 and 2, respectively. Carbonation of suspensions was carried out in an absorber (diameter 55 mm, height of water column 60 mm) equipped with magnetic stirrer for achieving better interfacial contact and a sintered glass gas distributor (diameter of pores 100 µm) using model gases I (15% CO_2 in air) and II (15% CO_2 and 0.035%SO_2) (9). CO_2 binding degree (BD_{CO2}) was calculated by the change in the content of CO_2 in the samples:

$$BD_{CO2} = CO_2/CO_{2\ max}*100, \% \hspace{3cm} (1)$$

where CO_2 is analytically determined CO_2 content in the sample in current time, %

$CO_{2\,max}$ is maximal possible CO_2 content in sample calculated on the base of free CaO in the initial sample, % The latter was calculated as:

$$CO_{2\,max} = \frac{CaO^i_{free} * M_{CO2}/M_{CaO} + CO^i_2}{100 + (CaO^i_{free}*M_{CO2}/M_{CaO})} *100, \% \qquad (2)$$

where CaO^i_{free} and CO^i_2 are the content (%) of free CaO and CO_2 in the initial sample, respectively. All indicators used are calculated on dry bases.

Table 1: Composition of Fly Ash Formed at Oil Shale Combustion[*]

Compo-nent	Con-tent, %	per kg oil shale	
		g	mol
CaO	46.11	210.6	3.76
SiO_2	33.70	153.9	2.56
MgO	1.99	9.1	0.23
Al_2O_3	9.26	42.3	0.42
Fe_2O_3	4.73	21.6	0.14
FeO	0.16	0.8	0.01
K_2O	3.57	16.3	0.17
Na_2O	0.46	2.1	0.034
Total	100.00	456.7	

Table 2: Composition of Flue Gas Formed at Oil Shale Combustion (amounts in moles per kg oil shale, air factor λ = 1.2

Compo-nent	From organic part	From mineral part	Total from organic and mineral part
CO_2	22.59	3.92	26.51
H_2O	16.98	–	16.98
N_2	136.70	5.08	141.78
O_2	6.04	0.22	6.26
SO_2	0.19	0.54	0.72 (~10.7 g/m^3)
SO_3	–	0.016	0.016
		Total	192.2 (~4.3 m^3 at STP)

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

Results and Discussion

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

In the calculations the amount of flue gas bubbled through the ash pulp was varied from 1 to 200 m^3/m^3 of pulp (solid: liquid ratio in the pulp was 1:17.5). The results indicated that the increase in the amount of flue gas is accompanied by essential changes in the equilibrium amounts of the system components (11). These data about Ca and Mg compounds is given on Fig1. 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:

$$CaSiO_3 + CO_2^{(g)} \leftrightarrows CaCO_3 + SiO_2 \qquad (3)$$
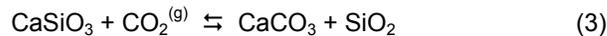
Thus, $Ca(OH)_2$ and $CaSiO_3$ are preferably used for $CaCO_3$ formation. After most of Ca is used to form $CaCO_3$ and the $CO_2^{(g)}$ binding potential is almost utilized, the formation of complex carbonates starts and some more $CO_2^{(g)}$ can be bound. Preferably $CaMg(CO_3)_2$ is formed, the amount of $CaCO_3 \cdot MgCO_3$ is some magnitudes lower. In forming complex carbonates almost all $Mg(OH)_2$ is used up. Also, 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 (10)). Binding products are $CaSO_4$ and Na_2SO_4; the amounts of other sulfates are negligible.

Figure 1: Equilibrium amounts of components (in moles per m³ of ash pulp) in the system of air – ash pulp depending on factor k (mole ratio of $CO_2^{(g)}$ contacted with the pulp and free CaO present in pulp): a – Ca compounds; b – Mg compounds; c – $CO_2^{(g)}$ derivatives
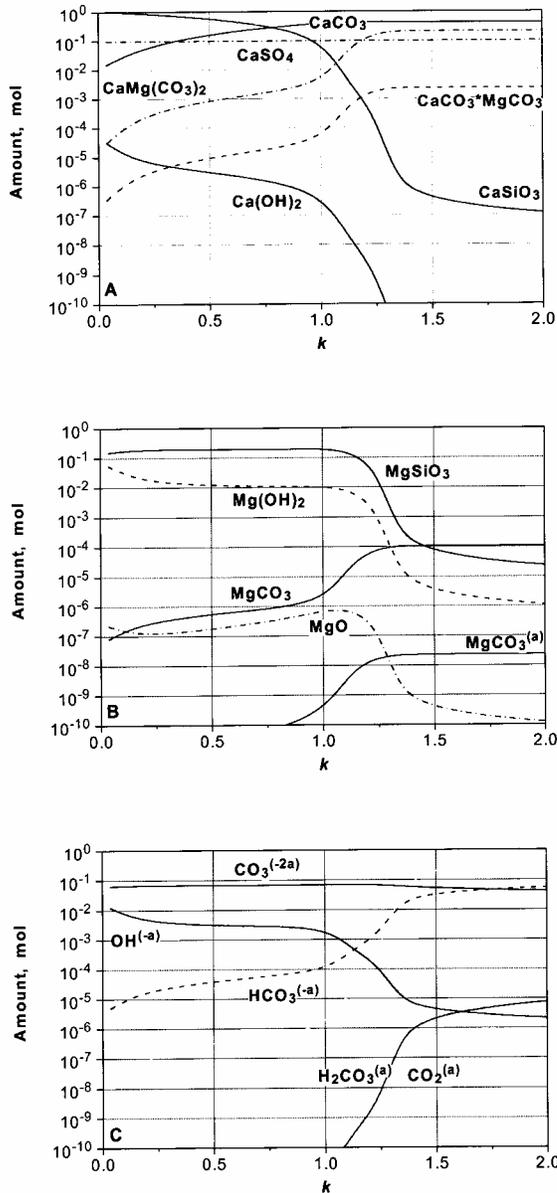
Carbonation of ash suspensions

Results of laboratory experiments for treating the suspensions of cyclone ash and pure CaO with gas 1 are presented on Fig. 2, 3 and 4. At the beginning of carbonation the suspension stayed deeply alkaline for a while (Fig.2). A rapid decrease in the pH value started at N ~3. The pH value decreased rapidly to 7 at one stage in the case of suspension of the lime. The decrease in the pH value was relatively slower in the case of ash - to ~9 at the beginning, and then slowly to 7, whilst the depth of carbonation (N) was significantly increased. The experiments indicated that the content of Ca^{2+}-ions changed similarly in both cases during carbonation, but the initial content of Ca^{2+}-ions was lower in the case of lime suspension (12). Probably, some components of the system oil shale ash – water are promoting saturation of the solution with Ca^{2+}-ions. The content of Ca^{2+}-ions decreased during carbonation synchronously with the content of OH⁻ ions and the pH value, but it started to increase again at pH values ~ 7.5 – 7 (Fig.3). It can be concluded, based on the results of chemical analysis of the solid phase, that the carbonation of the suspension of lime occurs faster than the carbonation of the suspension of cyclone ash: if the suspension of CaO achieved the value of binding degree of CO_2 90% and more at N = 2, then the suspension of cyclone ash at N = 3.5 – 4. Further treatment led to stabilization of the binding degree of CO_2 (BD_{CO2}) on the level of 96-97 %(Fig.4) In the case of suspension of ash, the binding degree reached up to 100% at N = 7 - 8. The dynamics in the content of CO_2 was similar, with the maximal value of 40 – 41% of CO_2 in the case of lime and ~15% in the case of ash. The results of experiments using gas II confirmed that in addition to CO_2, the suspension also binds actively SO_2 from the gas mixture. The content of SO_2 rose up to 2% in solid phase and up to 90 mg/l in liquid phase at N = 7. The value of binding degree of SO_2 (BD_{SO2}) showed that all SO_2 contacted with the suspension was bound by solid and liquid phase of the suspension. The calculations based on the results of chemical analysis of the products of laboratory experiments, indicated that the amount of CO_2 bound could reach up to 153.8 kg per 1 ton of oil shale ash or 70.8 kg per 1 ton of oil shale burnt in the process of electricity production. The annual amount of CO_2 bound by ash (according to the amount of oil shale burnt in the energy production in 2000, could reach up to ~730 000 tons (12).

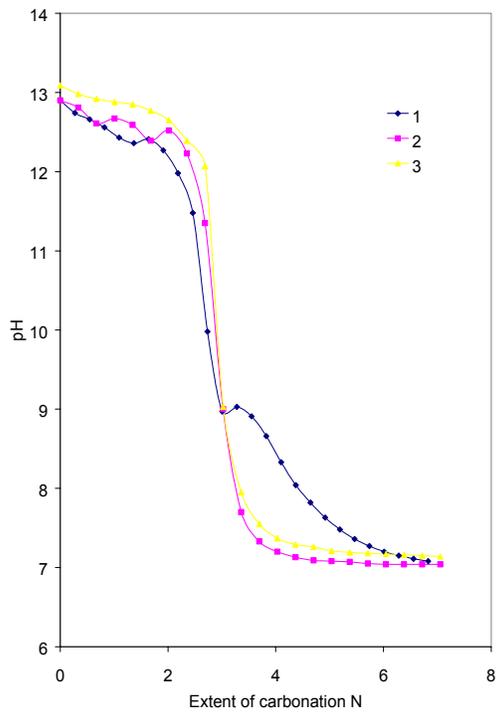Figure 2: Changes in pH versus extent of carbonation: 1 – cyclone ash (gas I), 2 – CaO (gas 1),3 – CaO (gas II).

Figure 3: Content of Ca^{2+} - ions in the liquid phase versus extent of carbonation N: 1 – cyclone ash (gas I), 2 – CaO (gas I), 3 – CaO (gasII)
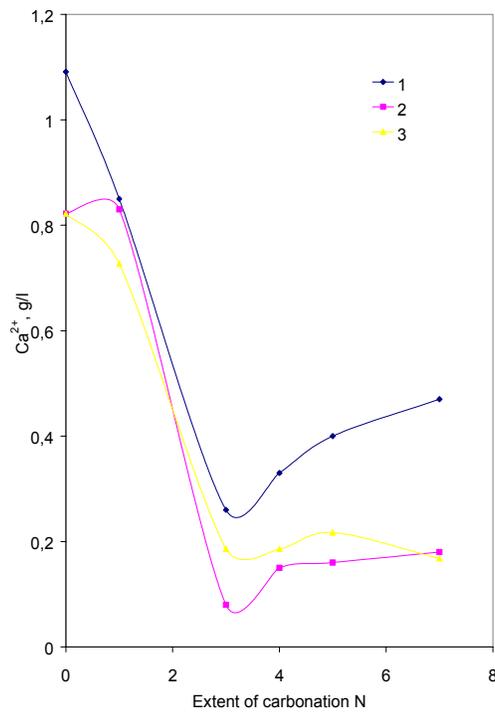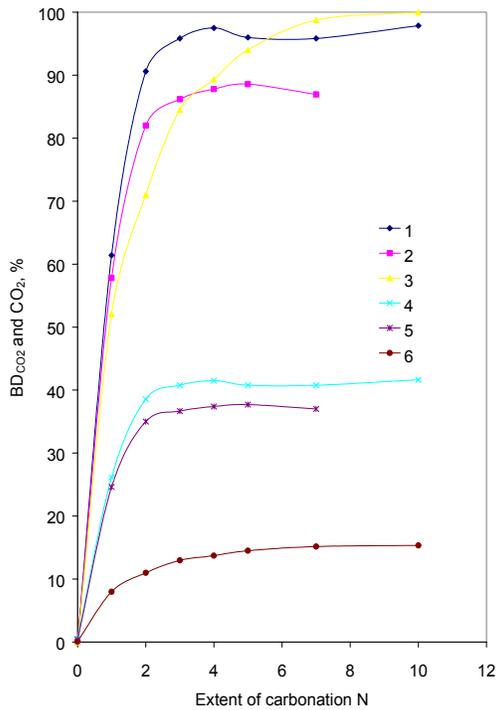

Figure 4: Dependence of CO_2 content (CO_2,%) and CO_2-bonding degree (BD_{CO2}) on the extent of carbonation N: 1-3 - BD_{CO2}: 1 – for CaO ini gas I, 2 – for CaO in gas II, 3 – for cyclone ash in gas I; 4-6 - CO_2: 4 – for CaO in gas I, 5 – for CaO in gas II, 6 – for cyclone ash in gas I

Conclusions

1. On the bases of the theoretical considerations and model experiments the possibility to abatement the CO_2 emissions formed at energetic utilization of Estonian oil shale has been shown. By treating ash - water suspensions with flue gases – the CO_2 binding capacity of the ashes could be completely utilized with formation mainly of $CaCO_3$. That can significantly decrease the CO_2 emission level as compared to the current situation.

2. By thermodynamical calculations 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 water suspension. A more deep decline in the equilibrium concentration of sulfur dioxide indicates its higher reaction ability, so, $SO_2^{(g)}$ is bound preferably. If equilibrium is reached, the $CO_2^{(g)}$-binding capacity of oil shale ash in the system flue gas – ash pulp (liquid – solid – gas) is completely utilized.

3. The experiments indicated that all the ashes bound actively CO_2 from flue gases whereas the binding rate of bottom ash was close to the binding rate of pure lime. The pH value of suspensions decreased to 7.5 – 7 during the carbonation process, thus, another environmental effect - chemical stabilization of alkali ash was achieved.

4. The high reactivity of SO_2 as compared to that of CO_2 in the case of their simultaneous existence in gas mixtures was proved. The suspension of lime bound SO_2 completely from flue gases forming $CaSO_3$.

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