

INTERACTIONS OF CHLORINE AND SULPHUR COMPOUNDS IN THE COKING PROCESSES OF COAL BLENDS

Andrzej R. KOSZOREK*, Małgorzata PALUCH and Mariusz MINKINA

Department of Chemical Technology of Coal and Petroleum, Faculty of Chemistry, Silesian University of Technology, 44-100 Gliwice, Krzywoustego 8, Poland, tel. +48 32 237 25 46

**Corresponding author's e-mail: ziutek@polsl.gliwice.pl (Andrzej R. KOSZOREK)*

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ABSTRACT

Chlorine and sulphur present in hard coal evolve during coal blend coking process in the similar range of temperatures and can interact between each other. These could also competitively interact with other components of a coal matter and crude coke-oven gas. In the piece of research impact of addition of selected sulphur compounds on chlorine emission in the process of laboratory coking of coal blends through determination of its content in produced cokes was observed. Significant impact of increase of sulphur content in the coal blend designed for coking on the amount of chlorine remaining in coke was found. Impact of increase of chlorine content in the coal blend designed for coking on the amount of sulphur remaining in coke was also observed. These phenomena show that interactions between chlorine and sulphur compounds do exist in the process of laboratory coking of coal blends.

KEYWORDS: cokemaking, chlorine emission, sulphur emission, interactions of chlorine and sulphur

INTRODUCTION

Elemental analysis of hard coals always shows simultaneous presence of sulphur and chlorine. Sulphur content varies within 0.1÷11% (Jasieńko, 1995) (in domestic coals within 0.5÷2.8%) (Wawrzynkiewicz, 1997), while chlorine content varies within 0.005 to above 1.2% (Hodges et al., 1983) (in domestic coals within 0.006÷1.89%) (Różkowska, 1987). Sulphur is present in hard coal in form of both inorganic and organic compounds. Inorganic sulphur is mainly in form of iron disulfide (FeS₂), as pyrite or, less frequently, marcasite. Presence of galena (PbS), sphalerite (ZnS) and chalcopyrite (CuFeS₂) has been detected in some deposits of hard coal. Low amounts of inorganic sulphur are also present in form of iron and calcium sulphates. Organic sulphur, being a component of organic coal matter, exists in form of thiophenic functional groups, aliphatic and aromatic thiols, sulphide and disulfide combinations. Elemental sulphur is present in coals sporadically, in low amounts (Gryglewicz et al., 1995; Jasieńko, 1995; Maes et al., 1997; Wawrzynkiewicz 1997).

Major mode of occurrence of chlorine in coal, as distinct from sulphur, is chloride anions in moisture anchored to the surface of micropores in coal macerals by organic ionic complexes, such as quaternary amine groups and alkali carboxyl complexes. Merely in coals with very high chlorine content (exceeding 0.8%) presence of crystalline chlorides, mainly halite (NaCl), was observed (Huggins and Huffman, 1995; Vassilev, 2000).

In the processes of coal carbonisation both chlorine and sulphur show high thermal mobility. During combustion of coal about 95% of sulphur contained in coal and about 90÷99% of chlorine are emitted to the atmosphere. Sulphur evolves mainly in form of sulphur dioxide (SO₂) and chlorine as hydrogen chloride (HCl) (Osborn, 1992, Łucoś, 1995;). During coking process of coal 30% to 70% of sulphur contained in coal blend abandon coke-oven chamber as a component of raw coke-oven gas – mainly in form of hydrogen sulphide (H₂S) (Gryglewicz, 1999). In the same time similar amount of chlorine – from 40% to 60% – passes from coal to crude coke-oven gas, mainly as hydrogen chloride (HCl). In temperature < 340°C takes place binding of evolved HCl with ammonia (NH₃) present in gas with formation of ammonia chloride (NH₄Cl) which is a major chlorine compound formed in the process. Amount of chlorine that remains in coke is, to the high extent, dependant on bonds between chlorine ions associated in coal's moisture and structure of coal under carbonisation. Formation of inorganic, non-volatile chlorine compounds such as NaCl, KCl, CaCl₂, complex silicates and aluminosilicates like sodalite Na₈[(AlSiO₄)₆Cl₂] or scapolite (Na,Ca)₄[Al₃(Si,Al)₃Si₆O₂₄(Cl,CO₃)] is of decisive importance. These compounds could be formed due to crystallization from ordinary water solution after evaporation of water, secondary reaction of chlorine ions contained in structure of coal being carbonised with components of mineral matter and reaction of HCl evolving in the process with mineral matter (Mia-

nowski and Koszorek, 1995; Koszorek and Mianowski, 1999).

Amount of sulphur remaining in coke is also dependant on forms of its presence in coal being carbonised. Significant role play also secondary reactions between original decomposition products originating from organic and inorganic combinations of sulphur with organic coal matter as well as mineral coal matter (Gryglewicz, 1999). Simultaneous presence of reactive chlorine and sulphur compounds in conditions of thermal coal processing can lead to their mutual interactions and also to competitive reactions with components of mineral matter of coal. Such interactions were observed in the process of combustion of coal. It was observed that increased content of chlorine in coal lowers SO₂ emissions, and presence of sulphur prevents formation of dioxins (Xie *et al.*, 1999).

EXPERIMENTAL

In the laboratory experiments that were carried out with the purpose to examine interactions between chlorine and sulphur compounds, two industrial coal blends were utilized in coking process. First of them, marked as *MK1* ($W_r^t=4.4\%$; $A^d=8.5\%$; $V^{daf}=37\%$; $SI=3.0$; $RI=55$; $Cl^a=0.35\%$; $S_t^a=0.57\%$) was composed of three coals of the 34 type (hard coal mine: „Krupiński”, „Anna” and „Szczygłowice”) and used for production of industrial coke in stamp charging system. The second coal blend, marked as *MK2* ($W_r^t=8.0\%$; $A^d=6.4\%$; $V^{daf}=28\%$; $SI=8.0$; $RI=80$; $Cl^a=0.32\%$; $S_t^a=0.63\%$) was composed of four coals of the 35 type (hard coal mine: „Borynia”, „Zofiówka”, „Jas-Mos” and „Pniówek”) and used for production of blast-furnace coke in top charging system. Selected organic and inorganic sulphur compounds: hydrate of iron(III)sulphate(VI) $Fe_2(SO_4)_3 \cdot nH_2O$, pyrite FeS_2 , ferric sulphide FeS , diphenyl sulphide $C_6H_4SC_6H_4$, thionaphthene C_8H_6S elemental sulphur S were introduced in the amount of 1g to both coal blends in series of laboratory coking experiments. Addition of sodium chloride (NaCl) in the amount of 0.5g was also introduced to these coal blends.

The process of laboratory coking of prepared coal blends was carried out in a reaction vessel (retort) made of heat resistant steel (diameter 80 mm, height 80 mm) equipped with system for evacuation of gaseous products. Coal blend in the amount of 200g, prepared by way of weighing its individual components and thorough mixing, was poured into the retort and compacted with a 5kg rammer. The retort with a charge was placed in a muffle furnace and the process of laboratory coking was carried out. The process consists in heating the charge from ambient temperature, about 20°C, until final temperature of 1000°C is reached in a charge core. Temperature inside the furnace was about 1170°C. Temperature of 1000°C in a charge core was reached after 3 hours of heating in the furnace. The carbonised sample was kept in this temperature for 1 more hour. After that time the hot retort

was removed from the furnace and remained in ambient temperature for cooling down.

In the result of each experiment solid coke residue was obtained in the retort. Chlorine and sulphur content were determined in the obtained coke. Determination of chlorine content was carried out using a method according to English standards (British Standard Methods, 1942). This consists in: mineralisation of 5 g sample with Eschka mixture, treatment of mineralised sample with concentrated nitric acid and determination of chlorine ions Cl^- content using titration by Volhard method. Determination of sulphur content was carried out using method according to Polish Standard PN-81/G-04514.02 (Polish Standard, 1981). This consists in: combustion of 0.5 g sample in temperature of 1250 - 1350°C in a quartz tube under oxygene flow, adsorbing of created sulphur oxides in 1% hydrogen peroxide solution and determination of sulphur content using alkalimetric titration method.

RESULTS AND DISCUSSION

Results of determinations of chlorine and sulphur content in basic coal blends and in cokes obtained from these blends, as well as results of determination of these elements content in prepared coal blends containing selected additives of chlorine and sulphur compounds and in cokes obtained from these blends are shown in Tab.1 and Tab.2.

Laboratory coking of 200 g of the *MK1* coal blend (coals of the 34 type) containing 0.7 g of chlorine (0.35%) and 1.14 g of sulphur (0.57%) gives 134 g of coke containing 0.42 g of chlorine (0.31%) and 0.55 g of sulphur (0.41%). Thus 60% of chlorine and 48.2% of sulphur contained in coal blend remain in coke. For the *MK2* coal blend (coals of the 35 type), containing 0.64 g of chlorine (0.32%) and 1.28 g of sulphur (0.64%), coke yield amounts to 138 g. The coke contains 0.39 g of chlorine (0.28%) and 0.66 g of sulphur (0.48%). These amounts constitute 60.9% of chlorine and 51.6% of sulphur contained in coal blend. Introducing of 0.5 g of sodium chloride (NaCl) into basic blends, *MK1* and *MK2*, results in increase of chlorine content in the blends at 0.3 g (i.e. at 42.8%). Cokes obtained from these blends, compared to cokes from coal blends without additives, are characterized with increased content of both chlorine and sulphur. For the *MK1* blend with the addition of sodium chloride, which contained 1.0 g of chlorine (0.5%) and 1.14 g of sulphur (0.57%), obtained coke contained 0.46 g of chlorine (0.35%) and 0.59 g of sulphur (0.45%), which constitute 46.0% of the amount of chlorine and 51.7% of sulphur contained in the coal blend. Increase of sulphur content in coke at 7.3% occurred. For the *MK2* blend with addition of sodium chloride, which contained 0.94 g of chlorine (0.47%) and 1.28 g of sulphur (0.64%), obtained coke contained 0.43 g of chlorine (0.32%) and 0.74 g of sulphur (0.55%). These constitute 45.7% of the amount of chlorine and 57.8% of sulphur contained in the coal blend. Increase of sulphur content in coke at

Table 1 Results of determination of chlorine and sulphur content in cokes obtained as the result of coking the MK1 coal blend together with selected additives

Item	COAL BLEND MK1 (200 G)				COKE OBTAINED FROM MK1							
	Type and amount of additive	Chlorine content		Sulphur content		Yield U _K [g]	Chlorine content		Sulphur content		Remained in coke	
		C _{Cl}	M _{Cl}	C _S	M _S		c _{Cl}	m _{Cl} ¹⁾	c _s	m _S ²⁾	chlorine E _{Cl} ³⁾	sulphur E _S ⁴⁾
		[%]	[g]	[%]	[g]		[%]	[g]	[%]	[g]	[%]	[g]
1. None	0.35	0.70	0.57	1.14	134	0.31	0.42	0.41	0.55	60.0	48.2	
2. 0.5 g sodium chloride	0.50	1.00	0.57	1.14	132	0.35	0.46	0.45	0.59	46.0	51.7	
3. 1.0 g ferrous sulphide	0.35	0.70	0.76	1.51	130	0.30	0.39	0.60	0.78	55.7	51.7	
4. 0.5 g sodium chloride + 1.0 g ferrous sulphide	0.50	1.00	0.76	1.51	130	0.32	0.42	0.70	0.91	42.0	60.3	
5. 0.5 g sodium chloride + 1.0 g elemental sulphur	0.5	1.00	1.07	2.14	129	0.31	0.40	0.41	0.53	40.0	24.8	
6. 0.5 g sodium chloride + 1.0 g pyrite	0.5	1.00	0.84	1.68	132	0.30	0.40	0.41	0.54	40.00	32.1	
7. 0.5 g sodium chloride + 1.0 g iron(III)sulfate(VI)	0.5	1.00	0.66	1.31	128	0.31	0.40	0.48	0.61	40.0	46.6	
8. 0.5 g sodium chloride + 1.0 g thionaphthene	0.5	1.00	0.69	1.38	130	0.28	0.36	0.43	0.56	36.0	40.6	
9. 0.5 g sodium chloride + 1.0 g diphenyl sulfide	0.5	1.00	0.66	1.31	126	0.31	0.39	0.36	0.45	39.0	34.4	

Table 2 Results of determination of chlorine and sulphur content in cokes obtained as the result of coking the MK2 coal blend together with selected additives

Item	COAL BLEND MK2 (200 G)				COKE OBTAINED FROM MK2							
	Type and amount of additive	Chlorine content		Sulphur content		Yield U _K [g]	Chlorine content		Sulphur content		Remained in coke	
		C _{Cl}	M _{Cl}	C _S	M _S		c _{Cl}	m _{Cl} ¹⁾	c _s	m _S ²⁾	chlorine E _{Cl} ³⁾	sulphur E _S ⁴⁾
		[%]	[g]	[%]	[g]		[%]	[g]	[%]	[g]	[%]	[g]
1. None	0.32	0.64	0.64	1.28	138	0.28	0.39	0.48	0.66	60.9	51.6	
2. 0.5 g sodium chloride	0.47	0.94	0.64	1.28	134	0.32	0.43	0.55	0.74	45.7	57.8	
3. 1.0 g ferrous sulphide	0.32	0.64	0.83	1.65	140	0.27	0.38	0.87	1.22	59.4	73.9	
4. 0.5 g sodium chloride + 1.0 g ferrous sulphide	0.47	0.94	0.83	1.65	140	0.29	0.41	0.67	0.94	43.6	57.0	
5. 0.5 g sodium chloride + 1.0 g elemental sulphur	0.47	0.94	1.14	2.28	138	0.28	0.39	0.45	0.62	41.5	27.2	
6. 0.5 g sodium chloride + 1.0 g pyrite	0.47	0.94	0.91	1.82	138	0.28	0.39	0.37	0.51	41.5	28.0	
7. 0.5 g sodium chloride + 1.0 g iron(III)sulfate(VI)	0.47	0.94	0.73	1.45	137	0.28	0.38	0.53	0.72	40.4	49.7	
8. 0.5 g sodium chloride + 1.0 g thionaphthene	0.47	0.94	0.76	1.52	137	0.27	0.37	0.40	0.55	39.4	36.2	
9. 0.5 g sodium chloride + 1.0 g diphenyl sulfide	0.47	0.94	0.73	1.45	137	0.27	0.37	0.48	0.66	39.4	45.5	

12.1% occurred. This situation shows analogy to the process of coal combustion in which increasing of chlorine content in fuel also resulted in decrease of sulphur compounds emissions (Xie *et al.*, 1999).

In all of the experiments of laboratory coking of coal blends that were carried out on blends with addition, in form of individual additives, inorganic and organic sulphur compounds in the amount of 1 g, fall of chlorine content in obtained cokes was found. The additives were chosen this way they contain groups characteristic to the forms of the relevant element present in hard coal. Addition of 0.5 g of sodium chloride (NaCl) was applied together with sulphur compounds to the majority of tested blends in order to observe more clearly the interactions between chlorine and sulphur compounds in the process under investigation. The results allow to state that the lowest decrease of chlorine content in coke was caused, for both coal blends, by the addition of ferrous sulphide (FeS). It is the sulphur compound having high thermal stability in conditions of the process under investigation, usually formed during carbonisation from decomposition of pyrite contained in coal.

In case of the MK1 coal blend with additive of 0.5 g of NaCl, chlorine content in coke fell down from 46.0% to 42.0%, i.e. at 8.7%, and in case of the MK2 coal blend, also chlorine enriched, chlorine content in coke fell down from 45.7% to 43.6%. This is a drop at 4.7% compared to coke obtained from the blend only chlorine enriched. Higher effect on increasing chlorine compounds emissions in the process of laboratory coking of coal blends and thereby on decreasing of chlorine content in coke, had other additives containing sulphur in inorganic form (elemental sulphur, pyrite and iron(III)sulphate(VI)-9H₂O). For the MK1 coal blend with addition of 0.5 g of NaCl, after introducing above mentioned additives, decrease of chlorine content in obtained cokes was 13%, and for the MK2 coal blend, with the same addition of NaCl the decrease was 9÷11% (compared to cokes obtained from these blends only chlorine enriched). The highest effect on the amount of chlorine remaining in coke in the process under investigation had additions of organic sulphur compounds. For the MK1 coal blend, chlorine enriched, addition of thionaphthene caused decrease of chlorine content in coke at as much as 21.7%, and addition of diphenyl sulphide – at 15.2%. For the MK2 coal blend, chlorine enriched, the drop of chlorine content in cokes obtained with addition of the same organic sulphur compounds was 14% in both cases.

While analysing obtained results it could be noted that introducing sulphur compounds, thermally unstable in conditions of the process under investigation (elemental sulphur, pyrite and iron(III)sulphate(VI)-9H₂O, thionaphthene, diphenyl sulphide), into coal blends subjected to coking do not result in increase of sulphur content in obtained cokes.

CONCLUSIONS

Interaction between chlorine and sulphur compounds, present in crude coke oven gas and/or being components of organic and inorganic coal matter, occur in conditions of laboratory coking process of coal blends.

Increasing of chlorine content in coal blends results in increase of sulphur content in cokes obtained from these blends. Chlorine content in cokes is also increasing.

Increasing of sulphur content in coal blend, regardless from its type, results in increase of chlorine emission during coking process, thus contributing into decreasing of chlorine content in coke. This effect is higher in case organic sulphur content is increased.

The observed interaction of chlorine and sulphur compounds in coking process should be taken into consideration while establishing composition of coal blends as this has an effect on quality parameters of obtained cokes – normalised content of sulphur and chlorine.

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