



**REACTIONS BETWEEN SODIUM AND SILICON
MINERALS DURING GASIFICATION
OF LOW-RANK COAL**

by

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In the loving memory of my dearest wife Barbara

*...ile Cię trzeba cenić
ten tylko się dowie kto Cię stracił...*

DECLARATION

This work contains no material which has been accepted for the award of any other degree or diploma in any university or any other tertiary institution, and to the best of my knowledge and belief contains no material previously published or written by any other person, except where due references has been made in the text.

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SUMMARY

Fluidised bed gasification (FBG) associated with integrated gasification combine cycle (IGCC) power generation is an important way of using vast low-rank coal resources in an economic and environmentally acceptable manner. A key factor in the successful operation of coal gasification systems is the ability to control and mitigate ash-related problems. Such problems are closely tied to the abundance and association of the inorganic components in coal and the gasification conditions. Of particular importance for low-rank coals is the presence of sodium, which has been found to cause FBG operational problems such as bed agglomeration and ash deposition. However, the critical fundamental mechanisms of sodium behaviour in coal gasification systems are not fully understood.

The main objective of this study was to elucidate the role of sodium and silicon minerals in formation of liquid phases potentially responsible for fluidised bed agglomeration during gasification of a high-sulphur low-rank coal in order to identify ways of preventing formation of those phases. Experimental investigations involved the preparation of synthetic coals, or separate mineral mixtures, with known quantities of organically-bound sodium or sodium chloride and silica or kaolin either separately or in combination. The mineral mixtures were used as an aid in the interpretation of the reactions of sodium with silica or kaolin in the coal char. In addition, thermodynamic predictions were made for the possible compositions and phase distribution of sodium and silicon species formed during gasification and pyrolysis of these synthetic coals.

The synthetic coals were pyrolysed and gasified in a horizontal tubular reactor under conditions representative of a typical fluidised bed gasifier. Other than mineral composition parameters, the reaction temperatures (650°C, 750°C and 850°C), gas environment (pure atmospheres of either nitrogen, carbon dioxide or steam) and reaction times (45 seconds to 35 minutes) were varied. Mineral mixtures were exposed to the same experimental conditions. The collected coal char and post-reaction mineral mixture products were analysed by wet chemical methods, electron microscopy and mineralogical methods.

The experimental program investigated sodium transformation and extent of vaporisation in each of the individual atmospheres. The organically-bound sodium was found to be transformed into sodium carbonate, contrary to thermodynamic predictions of the formation of sodium sulphide for pyrolysis conditions. Up to half of the sodium was vaporised from the char. Volatilisation of sodium increased with temperature and time, and was highest for gasification with carbon dioxide. Sodium chloride present in coal vaporised during pyrolysis and gasification and reacted with coal partly forming sodium carbonate. The release of sodium was disproportionate to that of chlorine. Almost all of the chlorine was released at 850°C, and its release was twice as high as sodium. The release of sodium and chlorine was dependent on temperature and time, but not on the particular gas atmosphere.

Steam was found, both theoretically and experimentally, to be the most important component of the gasification environment. Steam substantially reduced the melting temperature of sodium carbonate and consequently gasification with steam resulted in the formation, in a liquid-solid state reaction, of liquid silicates at as low as 750°C, while gasification with carbon dioxide resulted in the same at 850°C. Sodium chloride and silica reacted only in steam and formed fused silicates at 750°C, with the rate of silicate formation substantially slower than for reaction between silica and sodium carbonate. Formation of silicates around silica particles and fused silicate joints between individual silica grains inside the char was established to occur uniformly throughout char particles in gasification conditions. Liquid silicates would be a cause of bed agglomeration and defluidisation during fluidised bed gasification of coal.

Qualitative agreement was found for gasification but not for pyrolysis conditions between experimental results and thermodynamic predictions for the formation of liquid silicates from organically-bound sodium and silica, but at higher than predicted temperatures. The results for mineral mixtures were in better agreement with thermodynamic calculations as the rate of formation of silicates was much higher in mixtures than in the synthetic coal. The prediction by equilibrium calculations for all of the silica to be fully dissolved in liquid silicates was not observed under any of the experimental conditions. However, partial silica dissolution was concluded for mineral mixture products. Silica solubility in the formed liquid silicates will increase the total mass of fused silicate glass formed in a FBG.

Partial agreement has been established between theoretical predictions and experimental results for gasification and pyrolysis of coal with organically-bound sodium and kaolin. Experimental results showed that kaolin and sodium had reacted upon reaching 650°C to form a solid sodium aluminosilicate $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, principally nepheline with a melting point above 1250°C. The reaction rate was faster in steam than in carbon dioxide or nitrogen. Sodium chloride reacted with kaolin, but at a slower rate, also to form sodium aluminosilicate $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, with steam reaction rate much higher than in carbon dioxide. Increasing the process temperature increased the reaction rate.

It is inferred that under FBG temperature conditions, as kaolin is transformed with the preservation of its hexagonal crystal structure into meta-kaolinite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ it reacts with sodium into nepheline, with the further preservation of the hexagonal structure. Reactions of sodium with kaolin will prevent reactions of sodium with silica to form liquid silicates. No formation of sodium aluminosilicate albite $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ was established experimentally, contrary to thermodynamic predictions for both forms of sodium.

The results from experiments showed that carbon conversion in steam was considerably higher than in carbon dioxide for coals containing either form of sodium. It was established that coal activation energy is associated with catalytic activity of sodium. For coal containing sodium chloride, activation energies are substantially higher than for coals containing organically-bound sodium. The presence of such minerals as silica and kaolin significantly increases the activation energies for coal gasification reactions with steam and carbon dioxide. However, the impact was lower for coal containing sodium in the form of sodium chloride.

Recommendations made for future work include establishing efficient ways to introduce kaolin to low-rank coal during gasification to reduce the formation of liquid silicates and hence inhibit agglomeration and defluidisation.

TABLE OF CONTENTS

	Page
DECLARATION	iii
ACKNOWLEDGEMENTS	iv
SUMMARY	v
TABLE OF CONTENTS	viii
LIST OF TABLES	xiv
LIST OF FIGURES	xvii
1 INTRODUCTION	1
1.1 BACKGROUND	1
1.2 COAL GASIFICATION	2
1.3 SCOPE AND STRUCTURE OF THESIS	3
2 LITERATURE REVIEW	6
2.1 INTRODUCTION	6
2.2 INORGANIC MATTER IN COAL	6
2.2.1 Definition and Classification	7
2.2.2 Occurrence and Nature of Inorganic Matter	9
2.2.2.1 Minerals in coal	11
2.2.2.2 Sulphur	11
2.2.2.3 Chlorine	12
2.2.2.4 Sodium	14
2.2.2.5 Potassium	15
2.2.2.6 Calcium and magnesium	16
2.2.2.7 Silicon and aluminium	17
2.2.2.8 Iron	18
2.3 TRANSFORMATIONS OF INORGANIC MATTER DURING GASIFICATION	18
2.3.1 Chemical Transformations	19
2.3.1.1 Decomposition of the Inorganics during Pyrolysis	19
2.3.1.1.1 Sulphur transformations	23
2.3.1.1.2 Chlorine transformations	24
2.3.1.1.3 Transformations of the minerals	24
2.3.1.2 Transformations during Combustion	25
2.3.1.2.1 Sodium reaction with sulphur oxides	26
2.3.1.2.2 Sodium reaction with silica and aluminosilicates	26
2.3.1.2.3 Chlorine	30
2.3.1.2.4 Calcium, magnesium and iron	31

2.3.1.3	Transformations during Gasification	32
2.3.1.3.1	Sodium and potassium reactions	33
2.3.1.3.2	Alkali catalysed gasification	34
2.3.1.3.3	Potassium	35
2.3.1.3.4	Chlorine	36
2.3.1.3.5	Sulphur	37
2.3.1.3.6	Calcium and magnesium	38
2.3.1.3.7	Iron	39
2.3.1.3.8	Minerals	40
2.3.1.4	HTW Gasification Process Experience	42
2.3.1.5	Laboratory Gasification Experiments	44
2.3.1.6	Thermodynamic calculations	45
2.3.2	Physical Transformations	46
2.3.2.1	Mineral salt crystallisation	47
2.3.2.2	Melting and sintering	47
2.3.2.3	Vaporisation of inorganic and minerals	50
2.3.2.4	Ash coalescence	51
2.3.2.5	Char porosity	51
2.3.2.6	Particle temperature	52
2.4	AGGLOMERATION and DEFLUIDISATION	52
2.4.1	Agglomeration mechanisms	53
2.4.2	Agglomeration in spouted fluidised beds	55
2.4.3	Sintering and agglomeration	57
2.4.4	Slag viscosity	62
2.4.5	Defluidisation	62
2.4.6	Deposition	62
2.5	SUMMARY	63
2.6	OBJECTIVES OF THE PRESENT STUDY	70
3	THERMODYNAMIC CONSIDERATIONS	72
3.1	INTRODUCTION	72
3.2	OBJECTIVES	73
3.3	PREDICTION OF EQUILIBRIUM COMPOSITIONS	73
3.3.1	Computational method	74
3.3.2	Reaction system	75
3.3.3	System assumptions and limitations	76
3.4	DISTRIBUTION OF SODIUM SPECIES AT EQUILIBRIUM CONDITIONS	77
3.4.1	Coal containing organically-bound sodium	77
3.4.1.1	Effect of nitrogen and hydrogen atmosphere	77
3.4.1.2	Effect of carbon monoxide atmosphere	78
3.4.1.3	Effect of steam atmosphere	79
3.4.1.4	Effect of carbon dioxide atmosphere	79
3.4.2	Coal containing sodium as sodium chloride	79
3.4.3	Coal containing organically-bound sodium and kaolin	80
3.4.4	Coal containing sodium chloride and kaolin	81
3.4.4.1	Effect of nitrogen atmosphere	81
3.4.4.2	Effect of carbon monoxide atmosphere	82
3.4.4.3	Effect of steam atmosphere	83

3.4.4.4	Effect of carbon dioxide atmosphere	83
3.4.4.5	Effect of hydrogen atmosphere	84
3.4.5	Coal containing organically-bound sodium and silica	84
3.4.6	Coal containing sodium chloride and silica	85
3.4.6.1	Effect of nitrogen atmosphere	86
3.4.6.2	Effect of steam atmosphere	87
3.4.6.3	Effect of carbon dioxide atmosphere	87
3.4.6.4	Effect of hydrogen atmosphere	87
3.4.6.5	Effect of carbon monoxide atmosphere	88
3.4.7	Silicon distribution	88
3.4.7.1	Coal containing organically-bound sodium and silica	88
3.4.7.2	Coal containing sodium chloride and silica	88
3.4.7.3	Coal containing organically-bound sodium and kaolin	88
3.4.7.4	Coal containing sodium chloride and kaolin	89
3.5	SUMMARY	90
4	EXPERIMENTAL WORK	93
4.1	INTRODUCTION AND OBJECTIVES	93
4.2	COAL PREPARATION	94
4.2.1	Coal leaching technique	96
4.2.2	Choice of specific compositions for preparation of synthetic coals	96
4.2.3	Preparation of coal samples	97
4.2.3.1	Preparation of dried coal granules	99
4.2.4	Preparation of mineral mixtures	100
4.3	EXPERIMENTAL APPARATUS	101
4.4	EXPERIMENTAL PROCEDURE	104
4.5	ANALYTICAL METHODS FOR COAL AND REACTION PRODUCTS	106
4.5.1	Solubility of sodium and silicates	106
4.5.1.1	Staged water leaching analysis	108
4.5.1.2	Confirmation of sodium forms in prepared synthetic coals	108
4.5.2	FT-IR analysis	109
4.5.3	Electron Microscopy	110
4.5.4	Mineralogical X-Ray diffraction analysis	111
4.6	SUMMARY	111
5	TRANSFORMATIONS OF SODIUM IN HIGH-SULPHUR LIGNITE DURING PYROLYSIS AND GASIFICATION – EXPERIMENTAL RESULTS	114
5.1	INTRODUCTION	114
5.1.1	Transformations of organically-bound sodium.	115
5.2	OBJECTIVES	118
5.3	PYROLYSIS AND GASIFICATION OF COAL CONTAINING ORGANICALLY-BOUND SODIUM	119
5.3.1	Sodium volatilisation during pyrolysis and gasification	120
5.3.1.1	Sodium volatilisation during pyrolysis	120

5.3.1.2	Sodium volatilisation during gasification with carbon dioxide	122
5.3.1.3	Sodium volatilisation during gasification with steam	123
5.3.2	Solubility of sodium present in pyrolysis and gasification char	126
5.3.2.1	Effect of pyrolysis	126
5.3.2.2	Effect of gasification	129
5.3.3	Mechanism of formation of volatile sodium	130
5.3.4	Determination of sodium forms in pyrolysis and gasification char	132
5.3.4.1	Determination of sodium carbonate using FT-IR spectroscopy	132
5.3.4.1.1	Effect of pyrolysis	134
5.3.4.1.2	Effect of gasification	134
5.3.4.2	Determination of sodium carbonate by XRD technique	135
5.3.4.3	Determination of compounds between sodium and sulphur	135
5.4	PYROLYSIS AND GASIFICATION OF COAL CONTAINING SODIUM CHLORIDE	137
5.4.1	Sodium and chlorine volatilisation during pyrolysis and gasification	138
5.4.1.1	Effect of pyrolysis	138
5.4.1.2	Effect of gasification	140
5.4.2	Determination of sodium carbonate in char	143
5.5	SUMMARY	145
6	REACTIONS OF SODIUM WITH SILICA DURING PYROLYSIS AND GASIFICATION OF COAL – EXPERIMENTAL RESULTS	148
6.1	INTRODUCTION	148
6.1.1	Silicate formation and associated agglomeration and defluidisation	148
6.1.2	Formation and properties of silicate glass	150
6.2	OBJECTIVES OF THIS WORK	153
6.3	SILICA AND ORGANIC SODIUM MIXTURE	153
6.3.1	Chemical Analyses	153
6.3.1.1	Results for nitrogen atmosphere experiments	154
6.3.1.2	Results for carbon dioxide atmosphere experiments	156
6.3.1.3	Results for steam atmosphere experiments	158
6.3.2	Evaluation of formation of silicates	161
6.3.2.1	Effect of carbon dioxide and nitrogen atmosphere	161
6.3.2.2	Effect of steam atmosphere	164
6.3.3	Microscopic examination for formation of silicates	166
6.3.3.1	Effect of nitrogen atmosphere	167
6.3.3.2	Effect of carbon dioxide atmosphere	167
6.3.3.3	Effect of steam atmosphere	170
6.4	PYROLYSIS AND GASIFICATION OF COAL CONTAINING SILICA AND ORGANIC SODIUM	177
6.4.1	Chemical Analyses of Char	177
6.4.1.1	Results for pyrolysis char	178

	6.4.1.2	Results for gasification with carbon dioxide	180
	6.4.1.3	Results for gasification with steam	181
	6.4.1.4	Sodium volatilisation during gasification	184
	6.4.2	Microscopic examination of char	186
	6.4.2.1	Silicate formation during coal pyrolysis	186
	6.4.2.2	Silicate formation during gasification with carbon dioxide	187
	6.4.2.3	Silicate formation during gasification with steam	190
6.5		SILICA AND SODIUM CHLORIDE MIXTURE	194
	6.5.1	Formation of Silicates in Steam Atmosphere	194
	6.5.2	Microscopic examination	197
6.6		PYROLYSIS AND GASIFICATION OF COAL CONTAINING SILICA AND SODIUM CHLORIDE	200
	6.6.1	Pyrolysis in nitrogen	201
	6.6.2	Gasification with carbon dioxide	202
	6.6.3	Gasification with steam	202
6.7		SUMMARY	204
	6.7.1	Reactions between silica and organic sodium in mineral mixture	204
	6.7.2	Pyrolysis and gasification of coal containing organically-bound sodium and silica	205
	6.7.3	Reactions between sodium chloride and silica	207
7		REACTIONS OF SODIUM WITH KAOLIN DURING GASIFICATION AND PYROLYSIS OF COAL - EXPERIMENTAL RESULTS	208
7.1		INTRODUCTION AND OBJECTIVES	208
7.2		KAOLIN AND ITS THERMAL TRANSFORMATION	209
7.3		KAOLIN AND ORGANIC SODIUM MIXTURE	211
	7.3.1	Mineralogical analysis	211
	7.3.1.1	Products of thermal decomposition of kaolin	211
	7.3.1.2	Results for carbon dioxide atmosphere experiments	211
	7.3.1.3	Results for steam atmosphere experiments	212
	7.3.2	Chemical analyses of reaction products	214
	7.3.2.1	Solubility of kaolinite and its transformation products	214
	7.3.2.2	Solubility of reaction products	216
	7.3.2.2.1	Solubility in cold water	216
	7.3.2.2.2	Solubility in hot water	218
	7.3.2.3	Formation of sodium silicates	220
	7.3.3	Microscopic examination	221
7.4		PYROLYSIS AND GASIFICATION OF COAL CONTAINING KAOLIN AND ORGANIC SODIUM	225
	7.4.1	Chemical Analyses of Char	225
	7.4.2	Microscopic examination of char	228
	7.4.3	Mineralogical examination	231
7.5		KAOLIN AND SODIUM CHLORIDE MIXTURE	231
	7.5.1	Chemical Analyses	232
	7.5.2	Microscopic examination	235
	7.5.3	Mineralogical examination	236

7.6	PYROLYSIS AND GASIFICATION OF COAL CONTAINING KAOLIN AND SODIUM CHLORIDE	236
	7.6.1 Chemical Analyses of Char	237
	7.6.2 Mineralogical examination	238
	7.6.3 Microscopic examination	238
7.7	SUMMARY	243
8	KINETICS OF COAL GASIFICATION	246
8.1	INTRODUCTION	246
8.2	MECHANISM OF CATALYTIC GASIFICATION	246
	8.2.1 Catalytic effect of sodium on coal gasification	247
8.3	GASIFICATION KINETICS OF COAL	250
8.4	SUMMARY	256
9	GENERAL DISCUSSION	258
9.1	INTRODUCTION	258
9.2	SODIUM TRANSFORMATIONS	258
	9.2.1 Vaporisation of Sodium	259
9.3	REACTIONS OF SODIUM WITH SILICA	261
9.4	REACTIONS OF SODIUM WITH KAOLIN	264
9.5	IMPLICATIONS FOR AGGLOMERATION	266
10	CONCLUSIONS AND RECOMMENDATIONS	268
10.1	CONCLUSIONS	268
	10.1.1 Thermodynamic Studies	268
	10.1.2 Transformations of Sodium	269
	10.1.3 Reactions of Sodium with Silica during Gasification of Coal	270
	10.1.3.1 Reactions of silica and organically-bound sodium	270
	10.1.3.2 Reactions between sodium chloride and silica	271
	10.1.4 Reactions of Sodium with Kaolin during Gasification of Coal	272
	10.1.4.1 Reactions of kaolin and organically-bound sodium	272
	10.1.4.2 Reactions of kaolin and sodium chloride	273
	10.1.5 Kinetics of Coal Gasification	273
10.2	RECOMMENDATIONS FOR FUTURE WORK	274
	BIBLIOGRAPHY	276
