

**Waste Materials
Used in
Concrete Manufacturing**

Satish Chandra

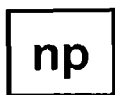
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WASTE MATERIALS USED IN CONCRETE MANUFACTURING

Edited by

Satish Chandra

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Göteborg, Sweden



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Preface

One of the most critical problems we face today is acid rain. One of the main causes is the burning of fossil fuels and, as a result, sulfuric acid and carbon dioxide are added to the atmosphere. These pollutant gases have detrimental effect on building materials. Thus there are two problems: 1) to decrease the gas emission, and 2) to produce construction material which is more durable to aggressive pollutant gases and acid rain.

The environmental aspects involved in the production and use of cement, concrete and other building materials are of growing importance. CO₂ emission, for example, is 0.8–1.3 ton per ton of cement production in dry process. SO₂ emission is also very high, depending upon the type of fuel used. Energy consumption is also very high at 100–150 kWt/ton of cement produced. It is costly to erect new cement plants. It costs approximately \$230 US per ton of installed capacity in Europe and \$230 US in developing countries. Substitution of waste materials will conserve dwindling resources and will avoid the environmental and ecological damages caused by quarrying and exploitation of the raw materials for making cement. To some extent, it will help to solve the problem otherwise encountered in disposing of the wastes. Partial replacement of clinker or Portland cement by slag, fly ash, silica fume, and natural rock minerals illustrates these aspects. Partial replacement by natural materials that require little or no processing, such as pozzolans, calcined clays, etc., saves energy and decreases emission of gases. The annual

Preface

production of Portland cement is more than 1000 M tons, while the output of waste materials suitable as cement replacement (slags, fly ashes, silica fumes, rice husk ash, etc.) is more than double this amount.

These waste materials can partly be used, or processed, to produce materials suitable as aggregates or fillers in concrete. These can also be used as clinker raw materials or processed into cementing systems. New grinding and mixing technology will make the use of these secondary materials simpler. Developments in chemical admixtures (superplasticizers, air-entraining agents, etc.) help in controlling production techniques and in achieving the desired properties in concrete.

The use of waste products is not only a partial solution to environmental and ecological problems. It significantly improves the microstructure, and consequently the durability properties of concrete, which are difficult to achieve by the use of pure Portland cement. The aim is not only to make the cements and concrete less expensive, but to provide a blend of tailored properties of waste materials and Portland cements suitable for a specified purpose. This however requires a better understanding of chemistry and materials science.

There is also an increasing demand for better understanding of material properties, as well as better control of the microstructure developing in the construction material, to increase durability. The combination of different binders and modifiers to produce cheaper and more durable building materials will be a factor in solving the ecological and environmental problems.

Göteborg, Sweden
January, 1997

Satish Chandra

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CONTENTS

1 PROPERTIES AND USE OF SOLID RESIDUE FROM FLUIDIZED BED COAL COMBUSTION 1

Jiri Brandštetr, Jaromir Havlica and Ivan Odler

INTRODUCTION	1
STARTING MATERIALS AND THE COMBUSTION PROCESS	3
Solid fuel	3
The Combustion Process	6
Chemical Reactions and Phase Transformations in the Course of Combustion	7
THE CHEMICAL AND PHASE COMPOSITION OF AFBC AND PFBC ASHES	12
THE REACTIVITY OF FLUIDIZED BED ASHES	20
THE ANALYSIS OF ASHES AND TESTING OF ASH MIXES ...	22
Loss on Ignition	22
Determination of Residual Carbon	23
Determination of CO ₂ of the Carbonates	23
Determination of Divalent Iron	23
Free Lime Determination	23
Determination of Sulfates	24
Pozzolanic Activity	24
Determination of Volume Stability	25

Contents

UTILIZATION OF ASHES WITHOUT ADDITIVES	25
PORTLAND FLY ASH CEMENTS AND COMPOSITE CEMENTS	28
POSSIBLE USE OF AFBC AND PFBC SOLID RESIDUE AS CONSTITUENTS OF CONCRETE MIXES	30
THE USE OF FLUIDIZED BED ASHES IN MULTI-COMPONENT PORTLAND CLINKER FREE CEMENTS	32
AUTOCLAVED PRODUCTS	34
ARTIFICIAL CONCRETE AGGREGATE	42
FLUIDIZED BED ASHES AS CONSTITUENTS OF PORTLAND CEMENT CLINKER RAW MEAL	43
LEGAL AND STANDARDIZATION ASPECTS, PERFORMANCE REQUIREMENTS	45
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH	46
REFERENCES	47

2 PRODUCTION AND USE OF BY-PRODUCT GYPSUM IN THE CONSTRUCTION INDUSTRY 53

Wojciech Roszczynialski , Marek Gawlicki and Wiesława Nocun-Wczelik

INTRODUCTION	53
CHEMICAL GYPSUMS	54
Phosphogypsums	55
Utilization of Other Chemical Gypsums	72
FLUE GAS DESULPHURIZATION PRODUCTS	74
Desulphogypsums	74
Fluidized Bed Desulphurization Products	87
Products from Other Desulphurization Installations	89
Utilization of the Flue Gas Desulphurization By-Products — General Remarks	93
Cementitious and Building Materials Produced With Flue Gas Desulphurization By-Products and Without Thermal Treatment	102
Binders and Building Materials from Dehydrated FGD Gypsum	114
Effect of Hydration Kinetics and Microstructure on the Properties of Hydrated Gypsum Materials	120
REFERENCES	130

3 FLY ASH IN CONCRETE 142

Aimin Xu

INTRODUCTION	142
FLY ASH CHARACTERIZATION	143
Chemical and Mineralogical Compositions and Structure of Fly Ash	148
Particle Size and Density of Fly Ash	151
EFFECT OF FLY ASH ON FRESH AND HARDENED CONCRETE PROPERTIES	153
Fresh Concrete	155
Hardened Concrete	158
DURABILITY	163
Freeze-Thaw Resistance	165
Sulfate Resistance	166
Alkali Aggregate Reaction	169
Steel Reinforcement Corrosion	170
Carbonation	172
OTHERS	174
REFERENCES	175

4 THE USE OF RICE HUSK ASH IN CONCRETE 184

Chao Lung Hwang and Satish Chandra

INTRODUCTION	184
Proper Disposal	184
Supplementary Binder	185
CLASSIFICATION OF RICE HUSK ASH	185
The Effect of Burning Temperature	187
The Effect of Burning Time & Furnace Environment	195
ANALYSIS OF THE QUALITY OF RHA	196
Different Sources	198
Different Processes	198
The Effect of Burning Time and Temperature on the Surface Area and Its Reactivity	201
HYDRATION MECHANISMS OF PASTE WITH RHA	201
Paste/RHA Heat Evolution Curve	201
Microstructure of Hydrated Cement Paste with RHA	203
Hydration Mechanisms of Paste with RHA	206

Contents

EARLY CHARACTERISTICS OF CONCRETE WITH RHA ..	211
The Workability of Fresh Concrete with RHA	211
The Setting Time of Concrete with RHA	213
The Compressive Strength and Impermeability of Concrete with RHA	214
The Modules of Elasticity, Creep and Shrinkage of Concrete with RHA	220
THE DURABILITY PROPERTIES OF CONCRETE WITH RHA	220
The Reduction in the Permeability of Concrete	222
Resistance to Thermal Cracking	222
Resistance to Alkali-Aggregate Reactions	222
Resistance to Acidic Attack	224
Resistance to Corrosion of Steel in Concrete	224
Resistance to Sulphate Attack	226
Resistance to Freezing and Thawing	227
SUMMARY	230
REFERENCES	231

5 BLAST FURNACE SLAG - THE ULTIMATE BINDER 235

Bob Talling and Pavel Krivenko

INTRODUCTION	235
GRANULATED BLAST FURNACE SLAG	236
General Characterization	236
Structure and Hydraulic Activity of Slags	242
PROCESSES OF HYDRATION AND HARDENING OF SLAG CEMENTS	248
Hydration of Slags	248
New Hydrate Formations in Slag Cements	250
CEMENTS USING BLAST FURNACE GRANULATED SLAGS	252
Clinker-Based Slag Cement	252
Non-Clinker Slag Cement	255
Slag Alkaline Cements	256
CONCRETES CONTAINING GRANULATED BLAST FURNACE SLAGS	259
Clinker-Based Slag Cement Concretos	259
Slag Alkaline Concrete or Alkali Activated Slag Concrete	263

FIELD EXPERIENCE AND SPECIAL USE OF SLAG	
ALKALI CEMENTS	277
CONCLUSIONS AND RECOMMENDATIONS	282
REFERENCES	283
 6 RED MUD AND PHOSPHOGYPSUM AND THEIR FIELDS OF APPLICATION	 290
<i>Wieslaw Kurdowski and Francois Sorrentino</i>	
INTRODUCTION	290
RED MUD UTILIZATION	292
Introduction	292
Characteristics of Red Mud	296
Utilization in the Building Industry	299
Aggregates and Lightweight Elements	305
PHOSPHOGYPSUM UTILIZATION	308
Introduction	308
Technologies of Wet Phosphoric Acid Production	310
Impurities in Phosphogypsum	313
Utilization of Phosphogypsum	316
Other Directions of Phosphogypsum Utilization	338
SUMMARY AND CONCLUSIONS	343
REFERENCES	344
 7 USE OF LIGNIN-BASED PRODUCTS IN CONCRETE	 352
<i>Ajoy Kumar Mullick</i>	
INTRODUCTION	352
Scope of the Report	353
THE NATURE AND SOURCE OF LIGNINS	353
LIGNOSULPHONATES	356
USE OF LIGNOSULPHONATES IN CONCRETE	360
Mechanisms of Action	362
Adsorption on Cement Particles and Electrical Repulsion ...	367
Rheological Aspects	373
EFFECTS ON HYDRATION OF CEMENT AND MICROSTRUCTURE OF CONCRETE	377
Hydration Characteristics of Cement	377
Microstructure	382

Contents

PERFORMANCE IN CONCRETE	386
Setting Time	387
Air Content	390
Effect on Workability and Slump Loss	391
Lowering of Water-Cement Ratio and Increase in Compressive Strength	394
FACTORS INFLUENCING THE PERFORMANCE OF LIGNOSULPHONATE ADMIXTURES	396
Cement Characteristics	398
Concrete Mix Proportions	402
Ambient Temperature	402
USE AS SUPERPLASTICIZERS	404
Development	404
Performance in Concrete	406
Applications in Concrete Containing Industrial Wastes ..	412
EFFECTS ON DURABILITY OF CONCRETE	415
CONCLUDING REMARKS	422
ACKNOWLEDGMENTS	423
REFERENCES	423

8 RECYCLING OF WASTE AS AN ALTERNATIVE RAW MATERIAL AND FUEL IN CEMENT MANUFACTURING 430

Hiroshi Uchikawa and Shunsuke Hanehara

INTRODUCTION	430
WASTE	431
Classification of Wastes	431
Types and Amounts of Wastes	433
Character of Wastes	436
Current Situations and Problems of Waste Treatment and Disposal	442
Problems	444
UTILIZATION OF WASTE AND ENVIRONMENTAL POLLUTION CONTROL	445
Reduction of Air Pollutants	448
Reduction of Dust	451
Reducing the Content of Harmful Elements	452
Reduction of Total Discharge by Energy and Resource Saving	454
Change of Control Level	460

INFLUENCE OF USING WASTE ALTERNATIVES TO REPLACE RAW MATERIALS AND FUEL ON CLINKER FORMATION AND THE CHARACTER OF CEMENT CLINKER	
CLINKER	463
Influence on Clinker Formation	464
Influence on the Character of Clinker	466
Apportionment of the Minor and Trace Elements to the Four Major Minerals by the Formation of Solid Solution	468
Amount of Clinker Minerals	477
Texture and Structure	477
Crystal Structure of Clinker Minerals	483
Pure Cement Compounds	484
Synthetic Clinker Minerals	488
Minerals in Commercial Clinker	491
INFLUENCE OF WASTE ALTERNATIVES ON CEMENT QUALITY	
QUALITY	492
Magnesium	495
Sulfur	501
Sodium and Potassium	508
Titanium	510
Phosphorus	510
Fluorine	512
Chlorine	513
Chromium	514
Manganese	515
Zinc	516
Strontium	518
Barium	519
Other Trace Elements	519
PROCEDURE TO USE WASTE AS ALTERNATIVE RAW MATERIALS AND FUELS	
MATERIALS AND FUELS	521
Principles of Waste Recycling	521
Establishment of Acceptance Inspection Standards of Waste and Application for Use to Administrative Agency	521
Development of Applied Technologies and Investment in Facilities	523
Expansion of Application Scope	527
Strict Control of Operation and Quality	531
Future Problems	531

Contents

OTHER TYPES OF CEMENT-UTILIZING WASTE	533
Alinite Cement	533
Blended Cement with Incineration Ash of Urban Refuse as Blending Component	535
SUMMARY	539
REFERENCES	540

9 USE OF SILICA FUME IN CONCRETE 554

Satish Chandra and Leif Berntsson

INTRODUCTION	554
ORIGIN	554
SILICA FUMES AND SYNTHETIC SILICA	556
Silica Fumes	556
Properties of Silica Fume	558
Synthetic Silica	558
EVOLUTION OF HYDROGEN	563
POZZOLANIC REACTIVITY, HYDRATION AND MICROSTRUCTURE	563
Pozzolanic Reactivity and Hydration	563
Microstructure	567
DURABILITY PROPERTIES	586
Permeability	586
Sulfate Resistance	590
Alkali Silica Reaction	593
Freeze-Thaw Resistance	603
CONCLUDING REMARKS	613
REFERENCES	614

10 PALM OIL SHELL AGGREGATE FOR LIGHTWEIGHT CONCRETE 624

A. A. Abang Abdullah

INTRODUCTION	624
LIGHTWEIGHT CONCRETE	625
PALM OIL SHELL AGGREGATE	626
Agricultural Waste	626
Palm Oil Industry	626
Palm Oil Shells	627

LIGHTWEIGHT CONCRETE USING PALM OIL SHELLS ...	627
Lightweight Aggregates	627
Compressive Strength	628
Flexural Strength	628
Creep	631
Shrinkage	631
COMPARISON WITH OTHER AGRICULTURAL WASTES .	634
APPLICATIONS	635
ACKNOWLEDGMENTS	636
REFERENCES	636
 INDEX	 637

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1

PROPERTIES AND USE OF SOLID RESIDUE FROM FLUIDIZED BED COAL COMBUSTION

Jiri Brandštetr, Jaromir Havlica and Ivan Odler

INTRODUCTION

The combustion of coal is expected to be the most widely used source of energy for the production of electricity at least in the foreseeable future. In conventional power plants, the combustion of the fuel takes place at temperatures between about 1200-1700°C and the process is associated with the liberation of large amounts of sulfur oxide in addition to CO₂. Worldwide, millions of tons of SO₂ are generated in this way annually [1]. Thus, the necessity exists to reduce the emission of SO₂ and to clean the produced flue gases.

In recent years a variety of "clean" technologies for coal combustion were developed [2]. Out of these, technologies based on fluidized bed combustion found greatest acceptance [4-6]. Here, finely ground coal is burnt together with ground limestone, acting as a sorbent of sulfur dioxide, in a fluidized bed at temperatures of approximately 850°C. Under these conditions, the SO₂ produced in the combustion process remains absorbed in the ash and additional

Waste Materials Used in Concrete Manufacturing

cleaning of the flue gas is not necessary. It may be expected that large fraction of newly built power plants, especially those with a smaller or medium capacity will be based on this technology. Instead of limestone also dolomite may be employed as a sorbent which, however, is less suitable should the ash formed in the process be utilized, rather than disposed.

The solid residue of the fluidized combustion of bituminous or sub-bituminous coals differ distinctly in their chemical and phase composition from ashes produced in conventional power plants and due to their generally favorable properties the potential exists for their large scale utilization [7-18]. In fact, at a site in the Netherlands, solid mining residues are processed in a fluidized bed reactor to produce a good quality inorganic binder, while the electricity, produced simultaneously, is considered to be a by-product [19].

A factor supporting the general trend to utilize industrial by-products [1,15,17,19-26] is the gradual depletion of high quality raw materials in the world and the steadily increasing volume of waste of all kinds which must be disposed, unless it is utilized in a meaningful way. This necessitates the development of technologies aimed at the utilization and/or recycling of secondary raw materials.

The permanently increasing number of power plants employing fluidized bed combustion results in an increasing interest in the utilization of the formed ashes whose composition and properties may vary in a wide range, depending on the composition of the fuel used, on the quality and amount of sorbent and on the combustion technology employed.

Fluidized bed combustion may be done either under atmospheric pressure (Atmospheric Fluidized Bed Combustion, AFBC) or at elevated pressure (Pressurized Fluidized Bed Combustion, PFBC). The latter approach, developed only recently, is used only in three power plants of the world and there are no published data on the properties of formed ashes so far.

New materials require new testing procedures to assess their quality and possible utilization. Should they be used under industrial

Solid Residue from Fluidized Bed Coal Combustion

conditions, these methods must also be sufficiently simple to make the testing procedure acceptable [27].

To attain a wide acceptance of new materials, it is essential to publish information about their properties and potential uses. In the case of fluidized bed ashes produced in flue gas de-sulfurization, the steadily increasing costs of their disposal may also stimulate efforts to utilize them in different applications.

The prevailing majority of papers on fluidized bed combustion of coal published so far deals with the optimization of the combustion process and on the equipment to be employed. Several conferences were dedicated to these topics [4,5]. This chapter provides information on the composition and properties of the solid residue from fluidized bed combustion of coal using either the AFBC or PFBC technologies. Also discussed will be the potential uses of these materials. The aim of this report is to generate interest in these materials whose volume is expected to increase steadily in the coming years.

As products of fluidized bed combustion exhibit hydraulic and/or pozzolanic properties, their use as a binder may result in a reduced consumption of Portland cement whose production is associated with a significant consumption of energy. This in course may also contribute to a reduction of the CO₂ emission. A cooperation of power plant operators, ecologists, material scientists, civil engineers and also legislators will be required to achieve an acceptance and a wide use of fluidized bed combustion ashes.

STARTING MATERIALS AND THE COMBUSTION PROCESS

Solid fuel

Bituminous or sub-bituminous coal, lignite and even different waste products from coal mining [19,28] may be employed as fuels in the combustion process. It is obvious that the quality of the fuel

Waste Materials Used in Concrete Manufacturing

and in particular the composition of its inorganic fraction determines to a great degree the composition and quality of the produced ash. Bituminous coal is the fuel used most widely in the industry. Its ash content lies typically at around 8 to 15%. The sulfur content of different coals may also vary greatly, which requires in most instances a de-sulfurization, to keep the SO_2 content in the flue gas low enough. Occasionally fuels with a content of inorganic constituents of up to 50% are used which results in an increased volume of produced ash. Up to several hundred tons of ash may be produced per day in some units. On the other hand, a certain amount of inorganic constituents in the fuel is necessary to assure the formation of a fluidized bed.

The chemical composition of the produced ash is independent on the employed combustion technology whereas the phase composition may be affected considerably. The factor that affects greatly the phase composition of an ash is the temperature of combustion which in the case of fluidized bed technology lies at around 850 °C. Another factor that also determines both the chemical and phase composition of the final product is the quality and quantity of the sorbent intermixed with the fuel.

The coal in fluidized bed combustion must be ground to a fineness below 4 mm and the amount passing the sieve 0.5 mm is typically around 20% . Finely ground limestone is the sorbent most widely used for the sorption of sulfur oxide.

At the temperature existing in the fluidized bed, limestone decomposes and converts to highly porous calcium oxide (lime) which reacts with sulfur oxide produced in the oxidation of the fuel. It is assumed that sulfur oxide also reacts with ground limestone directly in a topochemical reaction. The sorbent is being interground with the fuel to an appropriate fineness. Sometimes water is added to the mix to produce a slurry of desired consistency.

Alternatively, dolomite may also be used as a sorbent of SO_2 instead of limestone. The selection of the sorbent is usually done depending on the local availability of the material. Magnesium carbonate present in dolomite together with calcium carbonate

Solid Residue from Fluidized Bed Coal Combustion

decomposes at a lower temperature, namely already at about 500 °C, while calcium carbonate in limestone decomposes at 700 - 800 °C. At temperatures existing in the fluidized bed, i.e. at 850 °C, magnesium oxide loses its reactivity and tends to react with sulfur oxide only incompletely. A significant fraction of it remains in the combustion residue in non-reacted form as crystalline periclase. Thus the content of free MgO in the product of combustion may often exceed 10% , if dolomite is used as a sorbent. Contrary to that, the periclase content of ashes produced by adding limestone to the coal rarely exceeds 2.5%. Periclase reacts in a very slow reaction with water yielding magnesium hydroxide $\text{Mg}(\text{OH})_2$ (brucite). As this reaction is associated with an expansion which may cause cracking of building materials made from high periclase ashes, the potential of using such ashes is limited. One area of possible uses of high MgO ashes is in agricultural applications [29,30].

The combustion temperature of 850°C used in fluidized combustion has been selected as at this temperature the absorption of sulfur oxide by the added sorbent is most effective. Under these conditions a separate de-sulfurization of the residual flue gas becomes unnecessary. To attain a sufficient binding of sulfur, however, the sorbent has to be added in an stoichiometric excess, to increase the effectiveness of the sorption process. Obviously, the actual amount of limestone that has to be introduced increases with increasing sulfur content of the fuel. An addition of 4% of limestone is typical, if a coal with a sulfur content of around one percent is used.

The extent to which the added sorbent affects the oxidic composition of the produced de-sulfurization residue will depend on the ash content of the fuel and also on the amount of sulfur present in the fuel and thus on the amount of limestone that had to be added to attain a sufficient de-sulfurization. Typically the amount of $\text{CaO} + \text{MgO}$ coming from the added sorbent represents about 8-15% of the total amount of the solid de-sulfurization residue, if a coal with an ash content of 15% is employed. If fuels are employed that contain a significant fraction of calcium carbonate among its constituents, the amount of added sorbent may be reduced accordingly. This may be

Waste Materials Used in Concrete Manufacturing

the case especially in sub-bituminous coals which contain up to 10% of calcium carbonate.

The Combustion Process

Most widely used technology at present in fluidized bed combustion of solid fuels is the AFBC process (atmospheric fluidized bed combustion). Another technology, the pressurized bed process PFBC, that has been developed by the ABB company in Sweden [3] is being employed presently only at three different sites worldwide. In the recent approach the combustion takes place at a pressure of around 1.2 MPa. This makes it possible to reduce the height of the fluidized bed reactor significantly.

In both the AFBC and PFBC processes the combustion takes place in a circulating fluidized bed in which the fuel returns repeatedly into the reactor. Under these conditions the overall time in which the combustion takes place may reach up to several hours. In the course of combustion the primary formed sulfur dioxide SO_2 is converted to anhydrous calcium sulfate CaSO_4 , anhydrite II. The oxidation of S^{+4} to S^{+6} is catalyzed by heavy metals present in the ash.

Due to the low burning temperature the reactors and cyclones employed in the AFBC and PFBC processes do not require any refractory linings. A cooling of the internal walls with water is sufficient. Nitrogen oxides NO_x are formed only from nitrogen bound within the organic constituents of the fuel. Thus, both the SO_2 and NO_x content in the flue gas, produced in these processes is very low, well below levels required by the existing specifications. Fine solid constituents present in the flue gas are being separated by appropriate gas filters and must be disposed to be utilized in a meaningful way.

Burning in a circulating fluidized bed results usually in a thorough oxidation of the organic constituents of the fuel, so that the content of residual carbon may be easily kept below 1. Only if the rate of combustion is intentionally reduced the carbon content in the residual ash may increase. The greatest part of residual carbon in the

Solid Residue from Fluidized Bed Coal Combustion

ash is present in an amorphous form and exhibits a large specific surface area. As a consequence of it the water requirement in the production of mortar or concrete may be increased if a high volume of fluidized bed ash with a significant carbon content is added to the mix.

The particle size distribution of the residual material produced in fluidized bed combustion varies in a wide range and fractions of different granulometry are precipitated and separated at different sites. The coarsest fraction is the bed ash which represents usually 30 to 40% of the total amount of the solids. About 60% of the solid material is separated in cyclones whereas the fine fraction precipitated in last electrostatic precipitators or hose filters rarely exceeds 5%. Figures 1-3 show the particle size distributions of different kind of ash fractions (PFBC, Finspong, Sweden). It is also noteworthy to mention that different fractions differ not only in their fineness, but also in chemical and mineralogical composition and thus may be suitable for different applications. Compositions of various ashes and fractions are given in Tables 1-3.

Different ash fractions exhibit also differences in their net and bulk densities and specific surface areas. From a comparison of the existing particle sizes and specific surface areas it is obvious that different ash fractions differ also greatly in their porosities. The exact values will depend on the quality of the employed fuel and the quantity and quality of the sorbent employed.

Chemical Reactions and Phase Transformations in the Course of Combustion

The main constituents of the inorganic part of bituminous and sub-bituminous coals are clay minerals (illite, kaolinite, montmorillonite, halloysite etc.) - up to 50% , quartz - up to 15% and then iron oxides (hematite, limonite, magnetite), iron sulfides (pyrite, markasite) and carbonates (calcite, dolomite, magnesite). The low content of calcium sulfate varies. Minor constituents include various

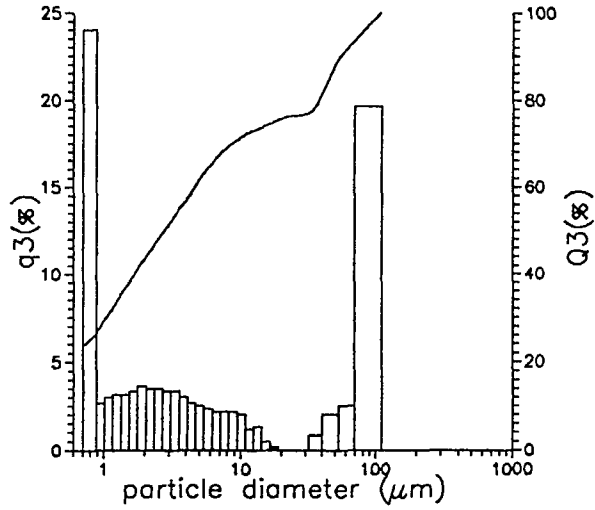


Figure 1. Particle size distribution (q3) and its integral curve (Q3) of PFBC ground bed ash: 25% < 0.97 μm, 60% < 5.00 μm, specific surface 7.96 m²/g (BET), specific gravity 2718 kg/m³.

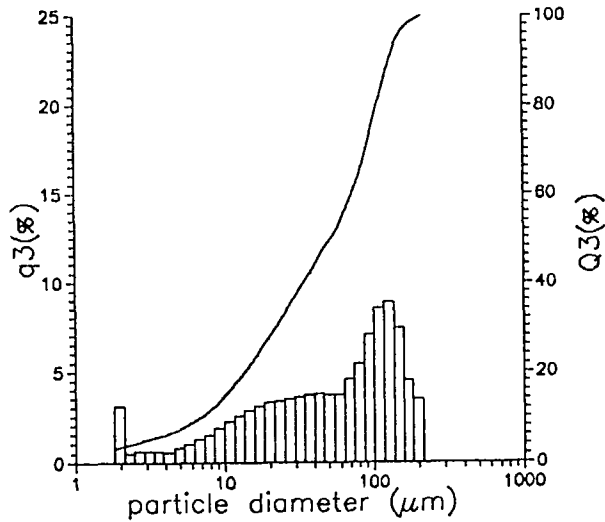


Figure 2. Particle size distribution (q3) and its integral curve (Q3) of PFBC cyclone fly ash: 25% < 15.1 μm, 60% < 53.6 μm, specific surface 4.72 m²/g (BET), specific gravity 2692 kg/m³.

Solid Residue from Fluidized Bed Coal Combustion

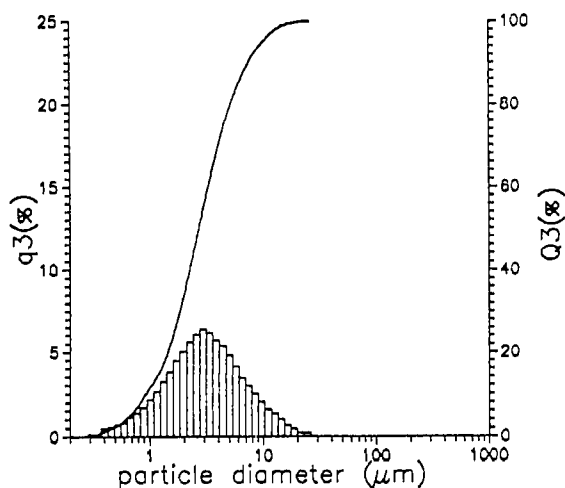


Figure 3. Particle size distribution (q_3) and its integral curve (Q_3) of PFBC filter fly ash: 25% < 1.46 μm , 60% < 3.46 μm , specific surface 6.39 m^2/g (BET), specific gravity 2580 kg/m^3 .

Table 1. Chemical Analysis of Individual Fractions of PFBC Ground Bed Ash (Finspong, Sweden). *L.O.I. = loss on ignition

	Percent Fraction, mm			
	<0.040	0.040-0.090	0.090-0.125	>0.125
SiO_2	23.4	40.3	42.5	49.8
CaO	34.0	21.2	18.6	13.5
MgO	2.0	2.3	2.6	2.5
Al_2O_3	9.4	13.7	15.5	17.0
Fe_2O_3	3.0	4.3	3.8	3.8
TiO_2	0.7	0.8	0.9	0.9
P_2O_5	0.2	0.2	0.3	0.2
MnO	0.1	0.1	0.1	0.1
Na_2O	0.7	0.9	0.8	0.8
K_2O	0.9	1.6	1.7	2.1
C	4.4	2.9	2.4	1.2
S	3.7	1.5	1.4	1.8
L.O.I.* (1000°C)	18.8	12.5	10.9	7.7

Waste Materials Used in Concrete Manufacturing

Table 2. Chemical Analysis of Individual Fractions of PFBC Cyclone Fly Ash (Finspong, Sweden).

	Percent Fraction, mm			
	<0.040	0.040-0.090	0.090-0.125	0.125-0.200
SiO ₂	36.8	37.0	33.7	31.7
CaO	17.3	21.6	26.6	29.5
MgO	3.7	3.5	3.3	2.9
Al ₂ O ₃	18.3	14.3	11.6	10.5
Fe ₂ O ₃	7.2	6.3	5.5	4.2
TiO ₂	1.1	1.0	0.8	0.7
P ₂ O ₅	0.3	0.3	0.2	0.1
MnO	0.2	0.2	0.2	0.1
Na ₂ O	1.0	0.9	0.6	0.6
K ₂ O	1.7	1.5	1.3	1.3
C	2.3	3.3	4.2	4.9
S	2.4	1.5	1.3	1.1
L.O.I. (1000°C)	7.9	11.2	14.9	17.5

Table 3. Chemical Analysis of Individual Fractions of AFBC Fly Ash (Trinec, Czech Republic).

	Percent Fraction, mm		
	<0.040	0.040-0.063	>0.063
SiO ₂	44.8	48.4	56.1
CaO	7.9	8.9	5.4
MgO	3.4	4.3	3.2
Al ₂ O ₃	22.5	21.0	22.6
Fe ₂ O ₃	7.4	6.3	5.3
TiO ₂	1.3	1.0	1.2
P ₂ O ₅	0.7	0.5	0.4
MnO	0.2	0.2	0.2
Na ₂ O	0.7	0.7	0.7
K ₂ O	2.4	2.6	2.4
C	4.3	0.9	0.2
S	1.1	1.7	0.7
L.O.I. (1000°C)	7.5	1.5	0.8

Solid Residue from Fluidized Bed Coal Combustion

phosphates, chlorides, humic acids and also free and chemically combined water.

The following chemical reactions take place in the course of coal burning in a fluidized bed in the presence of limestone: First, free water evaporates, followed by the escape of water bound within the clay minerals. The temperature of decomposition varies in different clay minerals: The interlayer water of halloysite escapes already at around 140°C, whereas its dehydroxylation starts at 450°C. Kaolinite loses its bound water at 500-650°C and converts to metakaolinite, which is an unstable highly reactive (x-ray amorphous) aluminum silicate with a large specific surface area. Montmorillonitic clays (bentonites) lose their water present in interlayer spaces at around 150°C; at this temperature the dehydration of sodium and potassium ions proceeds. At somewhat higher temperatures this is followed by an irreversible escape of water combined with cations of alkaline earths. Finally, at 600-700°C water bound as a constituent of the crystalline lattice is liberated. Illitic clays behave similar to montmorillonite, however, their decomposition proceeds more slowly and is often incomplete. The amorphous aluminosilicate phases and amorphous silicon dioxide, formed in the thermal decomposition of clay minerals, are responsible for the hydraulic and/or pozzolanic reactivity of the ashes seen after mixing them with water and other constituents.

Magnesium carbonate MgCO_3 decomposes at temperatures above 500°C and calcium carbonate CaCO_3 above 700°C. The rate of decomposition is accelerated if alkali ions are present. Pyrite decomposes at around 400-500°C and its decomposition is associated with an oxidation of the present sulfur and iron.

The calcium oxide produced in the decomposition of limestone exhibits a large surface and reacts readily with sulfur oxide formed in the combustion process in the temperature range 700-850°C. In the presence of excessive amounts of oxygen, anhydrite II (calcium sulfate, CaSO_4) rather than calcium sulfite CaSO_3 is formed as the final product of reaction. The excessive amount of the sorbent which was added to attain an effective de-sulfurization of the flue

Waste Materials Used in Concrete Manufacturing

gases, remains in the ash in the form of free lime (in the AFBC process) or calcium carbonate (in the PFBC process). To maintain a high reactivity of the produced fluidized bed ash it is important not to exceed significantly the combustion temperature of 850°C. This low temperature assures a higher specific surface area and thus a greater reactivity of this type of ashes as compared to ordinary fly ashes formed at combustion temperatures reaching 1600°C, when a liquid melt is formed. The final conventional fly ash consists mostly of spherical particles that contain, besides of the glass phase, also crystalline constituents such as mullite, anorthite or spinel. The pozzolanic reactivity of this ash is mainly due to the glass phase, whereas the majority of the formed crystalline phases is nonreactive. If coals containing calcium carbonate are utilized, also here calcium oxide is formed in its decomposition and reacts with SO₂ and O₂, yielding CaSO₄. However, non-reacted CaO stays in the ash as dead burnt lime. This phase, as well as free MgO, are undesirable constituents of fly ashes as they may react slowly with water, yielding hydroxides. This reaction may be associated with an expansion and cracking of materials produced from such ashes.

THE CHEMICAL AND PHASE COMPOSITION OF AFBC AND PFBC ASHES

The solid residue formed in the AFBC and PFBC processes may be considered to be blend of the inorganic fraction of the employed fuel, the compound of sulfur produced in the de-sulfurization reaction and of the excessive sorbent. Their oxidic composition may be estimated from the composition of the fuel, of the interblended sorbent and their mutual ratio. The chemical composition is similar to that of fly ashes received by conventional high temperature combustion of the same coal, except higher CaO (or MgO) and SO₃ contents (see Table 4).

The chemical composition of the ash alone does not suffice for assessing the quality and thus the potential uses of the material. In addition to the overall amount of present CaO it is important to

Solid Residue from Fluidized Bed Coal Combustion

Table 4. Chemical Composition (in oxides) of Bed Fly Ash [11,43].
(Compared to Ignited Samples).

	Bituminous Coal					Sub-bituminous Coal		
	Slag-tap boiler	Atmo- spheric fluidized bed FA	Pressurized fluidized PFBC solid residue Finspong			Slag-tap boiler	Atmospheric AFBC solid residue	
			Bed ash	Cyclone FA	Filter FA		Bed ash	FA
t, °C	>1300	<900	<900	<900	<900	>1300	<900	<900
SiO ₂	40-50	33-48	35.4	37.09	38.48	20-70	7-17	80
Al ₂ O ₃	23-35	13-20	12.88	15.63	23.39	1-15	4-6	0.5
Fe ₂ O ₃	4-17	5-10	3.34	6.02	6.86	1.5-20	8-10	1
CaO	1-8	8-18	23.49	20.29	10.12	8-40	36-47	11
MgO	0.8-4.8	1-2	1.62	2.71	2.70	0.5-7.0	8-9	1
K ₂ O	1.5-5.5	2-4	1.57	1.64	2.12	0.1-1.5	0.3-0.7	0.1
Na ₂ O	0.1-3.5	0.4-0.7	0.60	0.89	1.82	0.1-2.0	0.1-0.2	0.2
SO ₃	0.1-2.0	3-12	10.59	5.66	11.63	1.5-15	10-13	1.3
TiO ₂	0.5-1.3	0.5-1	0.60	0.60	1.39	0.1-1	-	-

distinguish between the amount present in the form of free lime and those bound within the existing calcium sulfate, calcium carbonate or clay mineral decomposition products. It also does not suffice to know the loss on ignition (as determined at 975°C in line with EN 196-2) as this value includes the amount of residual carbon, combined water and CO₂ bound within the present calcium or magnesium carbonate. It may also be important to distinguish between the divalent Fe²⁺ and trivalent Fe³⁺ forms of iron as the oxidation of the former is associated with an undesired expansion [43].