A NOVEL INSULATING CERAMIC POWDER DEVELOPED FOR APPLICATION IN THE MATERIALS INDUSTRY

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ABSTRACT

This paper presents results of an investigation aimed at synthesizing an insulating powder from industrial wastes from the Coal and Steel Industries.

Insulating powder is used to minimize heat losses in liquid steel – containing vessels like Ladles and Tundishes. They are mixtures of one or more refractory components, mixed with fast-burning materials. The results of the thermal conductivity tests were interesting, because they did not only show that the newly formulated powders had comparable thermal insulating properties with the imported ones but also suggested, by the clearly lower thermal conductivity values, that the locally- made materials might in fact be superior. It also worthy of note that the K-value of the coal – ash – based powder (0.12) was lower than that of the coal – reject – based on (0.135), thus the coal reject and coal ash based powders approximately corresponded in composition to imported samples I and II respectively (and also to compound types I and II respectively). This suggested that coal – ash should be used for the formulation of type I compounds and coal reject for type II compounds.

Preliminary results from chemical analyses and thermal conductivity tests compared favorably with data for imported insulating compounds. Thus a substitute for the usual proprietary and very costly insulating powder for use in steel and allied industries had been developed with the attendant huge savings in foreign exchange.

Key words:

Thermal conductivity, insulating, tundish, magnesite, ladle, coal – ash

BACKGROUD INFORMATION

Insulating powders are used to minimize heat losses in liquid steel – containing vessels like ladles and Tundishes. They are mixtures of one or more refractory components, mixed with fast burning materials. A brief description of the tapping and teeming processes during steel making is presented to illustrate the stage at which the insulating powder is applied:

(i) First, the molten metal is tapped along with slag into the ladle. At this point, the steel is agitated, and it moves turbulently in the ladle owing to a high rate of oxidation. Because a high percentage of dissolved oxygen results from these events, there is need for de-oxidation before ingot or continuous casting

(ii) For purposes of deoxidizing and alloying ferroalloys like ferrosilicon and ferromanganese are added depending on the type of steel required. The reactions that take place of the type:

$$(Mn) + (0) = Mn0$$
$$(Si) +2 (0) = Si0_2$$

With the conversion of the dissolved oxygen to stable oxides which are transferred into the slag phase, there is a drastic reduction in the dissolved oxygen level in the molten metal, and consequently there s a gradual reduction in the Turbulence in the steel. This results in the formulation of a metal – stag – gas emission layer. This layer permits passage of atmospheric oxygen through the porous slag to the molten metal without appreciable mass transfer between the slag and the molten metal

(iii) At this stage, the insulation powder is added. The fine powder stays at the surface layer of the slag, because of its low density, and burns off with the fusion of the refractory materials, thereby forming a thin protective layer which prevents heat transfer from the melt container and possible re-oxidation of the molten metal by atmospheric oxygen.

Steel industries consume large quantities insulating compound each year. These industries in most countries like Nigeria completely depend on importation of these powders, a situation which costs the countries huge sums of hard currency. In a cost benefit analysis recently carried out at a major steel industry in Nigeria (1) under its import – substitution research programmes; it was shown that large sums of hard foreign exchange can be saved if insulating powder can be developed from locally available materials. The analysis shows that the cost of imported insulating powder over a ten – year period was over $* 4,528,000.00 based on a consumption rate on 800 tonnes of the compound at $ 566.00 per tonne and for 500.00 tonnes of liquid steel per annum. The estimated cost of local production over a ten – year period, on the other hand, was less than $ 796,000.00 (1). Thus, if research efforts directed at the development of insulating powders from local industrial wastes are successful, the nation would be saving more than $ 3,704m, if one considers the extra costs of importing and handling. This estimate was made in 1985, if carried forward to the present and foreign exchange market era, the profit level indicated above would be quadrupled.

This report presents a novel idea conceived by the authors to develop good quality insulating compounds based on locally available coal-base waste materials. The coal-base materials are coal reject and burnt coal (coal ash), and other materials include calcium oxide and burnt magnesite bricks. The compounds developed have comparable compositions with those currently imported by Delta Steel Company Ltd. Warri in Nigeria and the results of a partial thermal characterization suggest comparable thermal performances in a pyrometallurgical environment.

2.0 CLASSIFICATION OF INSULATING POWDERS

Insulating powders may be classified into two main categories depending on application and effect.

i) High insulating (low thermal conductivity)

ii) Low insulating (high thermal conductivity)

Table 1 gives the approximate compositions of these two types of powders, where type 1 represents the "high insulating" type, and type II the "low insulating" type.

*$1 is equivalent to ₦140

Table 1
Approximate compositions of types I and II ladle covering powders

OXIDE/ELEMENT	OXIDE/ELEMENT	
	Type I%	Type II
S_iO_2	35.0	45.0
T_iO_2	0.50	1.0
Al_2O_3	17.77	15.0
Fe_2O_2	2.0	3.0
FeO	-	-
M_nO	0.05	0.2
CaO	10.20	8.6
MgO	11.5	20.0
$Na_2O + K_2O$	5	5
C (total)	15.0 – 20.0	5.0
Bulk relative Density	0.5 – 0.7	0.1.0.2

2.1.1 APPLICATION AND CHARACTERISTICS

2.1.2 **Type I:** The raw material basis for type I is flue dust. Insulating compounds of this class are applied in steel – making processes involving the manufacture of ingots and slabs over 5 tonnes; and for all plain and medium alloy steels. They have very good insulation qualities generally because of their low inclination to form slags.

2.1.3 **Type II:** The raw material basis for type II include specially treated minerals. They are used in steel – making processes involving the manufacture of ingots and slabs about 2 tones; for all plain and medium alloyed steels. They vitrify in the presence of casting fluxes. This type of insulating powders may therefore occasionally lose their insulating properties.

2.2 MAJOR CONSTITUENTS

Table I shows that insulating compounds (whether Type I or Type II) are essentially quaternary oxide systems of the type: CaO – AL_2O_3 – MgO – S_iO_2 (CAMS), with substantial amounts of elemental carbon and small amounts of the oxides Fe_2O_3, NaO/K_2O, and T_iO_2. Traces of other oxides such as MnO, BaO, P_2O_5 and SO_3 may also be present.

The quaternary system CaO – AL_2O_3 – MgO – SiO_2, which constitutes the key component of the insulating materials, has been extensively studied, especially with regard to thermodynamic stability phase relationships of the components, composition, and structure. The results of some of these studies are available in the literature (2 – 8).

3.0 MATERIALS AND METHODS:

3.1 Material Resources:

The base material used in this study is spent coal – coal reject and coal ash. The choice of these materials is based on a knowledge of coal chemistry. Also spend magnesite brick and limes (calcium oxide) were used for blending in appropriate proportions with the spent coal material. The coal reject used was collected from the Nigerian Coal Corporation, while the coal ash (burnt) was obtained from the Oji River power station all in Nigeria.. The burnt bricks and the calcium oxide were obtained from the Delta Steel Company, Aladja in Nigeria.

Imported insulating powder was also obtained from the Delta Steel Company for use as reference base for comparison.

3.2 Material Preparation

3.2.1: The insulating material is an aggregate of properly blended powders of several refractory oxides. The refractory powders are prepared by combination (crushing and coarse grinding) of bulk material, and by chemical methods involving solid state calcinations or vapour phase condensation. The methods of preparation of these powders are described in standard texts, but specific methods applicable to special situations are described in the literature (9 – 17). The final stages of powder preparation include comminution (fine grinding), screening, and blending or mixing. After preparation, the refractory powders often undergo further treatment prior to use as "refractories". The powder treatment here is designed primarily to control the rate of reaction of the unshaped refractory at given temperatures

The coal reject was crushed to coarse powder using a jaw crushing machine, and was later reduced to fine powder by a gyratory crushing machine operating for six process of grinding, but with a longer time of ten minutes in the gyratory crusher (18 – 20).

The burnt coal (coal ash) was dried in the sun for one day to drive off moisture in the ash. Subsequently, it was sieved through a 0.5mm mesh screen to remove lumps of un-burnt coal.

3.3 X-ray Chemical Analysis

Two different samples of imported insulating powder (Samples I and II) were chemically analyzed using X-ray techniques. Similarly, the coal ashes were chemically analyzed. The result of these analyses is presented in table II and III.

TABLE II
CHEMICAL COMPOSITIONS OF IMPORTED INSULATING POWDERS, SAMPLES I AND II

CONSTITUENT	COMPOSITION, WT. %	
	SAMPLE I	SAMPLE II
S_1O_2	34.60	51.12
Al_20_3	17.77	20.30
Ca0	11.66	10.55
Mg0	5.77	4.50
Fe_20_3	2.73	1.73
K_20	0.86	0.01
Na_20	0.03	0.05
Ba0	0.01	0.10
P_20_5	0.01	0.02
$S0_3$	0.05	0.07
T_10_3	1.50	1.02
Mno	0.30	0.04
Carbon (C)	8.23	5.30
Lost items	16.48	5.19

TABLE III
Chemical Composition of Coal Reject and Burnt Coat (coal ash)

CONSTITUENT	COMPOSITION, WT. %	
	SAMPLE I	SAMPLE II
S_1O_2	47.88	62.50
Al_20_3	24.10	29.00
Ca0	0.10	0.30
Mg0	0.00	0.0
Fe_20_3	1.96	2.50
K_20	0.03	0.60
Na_20	0.02	0.40
Ba0	0.03	0.10
P_20_5	0.06	0.10
$S0_3$	0.03	0.05
T_10_3	1.20	1.5
Mno	0.05	0.05
Carbon (C)	11.30	1.30
Lost items	13.24	1.6

4.0 DEVELOPMENT OF THE POWDER

Upon examination of the data of tables I and II, it was necessary to depress the Silica levels in the coal reject and the coal ash to bring them to levels appropriate to types I and II insulating powders respectively (see table II). In the same vein, it was considered necessary to introduce Magnesia (Mg0) by blending these spent coal materials with the burnt brick powder. The low level of Ca0 in the materials also made it necessary to introduce lime powder.

4.1 Insulating Powder Using Coal Reject:

Based approximately on the desired levels of $Si0_2$, Ca0 and Mg0, a blend of the following composition was prepared: (coal reject) 70 calcium oxide) 15 --- (4) the subscripts in Equation (4) refer to weight percent .from formula (4), it is clear that the anticipated percentage of a given constituent, say A, in the resulting blend would be given by:

% A (total) = 0.7 (% A in coal reject)

\+ 0.15 (%A in calcium oxide)

\+ 0.15 (% A in burnt brick) -------- 15

As a first approximation, we assume that the calcium oxide is pure, and that the burnt magnetic brick is also pure magnesia. These assumptions are not expected to be very exact. The anticipated composition of the resulting covering powder, generated from equation (5), is given in table IV

4.2 Development of insulating powder from coal ash burnt coal

In line with the approach described in section 4.1 above, an insulating powder based on coal ash was blended, with the suggested composition:

(Coal Ash) 70 (calcium oxide) 15 (Burnt Brick) 10 (Coal Dust) 5 --------------- (6)

The coal dust in formula (6) is pure coal in pulverized form, and has been added to make up for the shortage of elemental carbon in coal ash (see table III). The expected percentage of a given constituent, say B, in the blend would then be:

% B (total) = 0.7 (%B in coal ash)

\+ 0.15 (% B in calcium Oxide)

\+ 0.10 (% B in burnt brick)

\+ 0.05 (% B in coal dust) ----------- (7)

The same assumptions made in section 4.1 about the purity of calcium oxide and the magnesia of the burnt brick are made here, and in addition we assume that the coal dust is pure carbon. The composition of the resulting coal ash –based covering powder computed from equation (7), is also given in table IV.

TABLE IV
Composition of the developed coal reject and Coal Ash- based powder, derived from equations (5) and (7)

CONSTITUENT	COMPOSITION, WT. %	
	COAL REJECT COAL BASED POWDER	COAL ASH, OR BURNT BASED POWDER
S_1O_2	33.52S	43.75
Al_20_3	16.87	20.30
Ca0	15.07	15.21
Mg0	15.00	10.00
Fe_20_3	1.37	1.75
Ti^02	0.84	1.05
K_2^0	0.02	0.42
Na_20	0.01	0.28
Ba0	0.02	0.07
Mno	0.05	0.04
P_20_5	0.04	0.07
$S0_3$	0.02	0.04
Carbon (C)	7.91	5.91
Lost items	9.27	1.12

5.0 CHARACTERIZATION TESTS ON PROPOSED POWDERS

Preliminary characterization tests were carried out for purposed of:-

(i) Comparing the actual composition of the new powders with those of the imported powders

(ii) Comparing the heat insulation properties of the two sets of powders

For (i), the compositions of the various powders were obtained by X-ray analysis, while for (ii), it is found necessary to determine the thermal conductivities of the materials. A special technique was developed by the authors for the convenient measurement of the thermal conductivities of these powdery compounds.

6.0 RESULTS

(1) Composition

Table V presents the result of the X-ray analysis of the various powders. From the table, a quick comparison of the composition of the imported and locally developed powders can be made. It is

Constituent	Composition, Wt. %			
	Imported insulating powder		Insulating powder developed locally	
	Sample I	Sample II	From coal reject	From coal ash (burnt coal)
S_i0_2	34.60	51.12	34.86	45.34
Al_20_3	17.77	20.30	17.75	20.65
Ca0	11.66	10.55	12.32	12.49
Mg0	5.77	4.50	11.64	5.95
Fe_20_3	2.73	1.75	1.73	2.43
Ti^02	1.50	1.02	0.86	1.45
K_2^0	0.86	0.01	0.02	0.43
Na_20	0.03	0.05	0.01	0.07
Ba0	0.01	0.10	0.02	0.08
Mno	0.30	0.04	0.03	0.03
P_20_5	0.01	0.02	0.04	0.05
$S0_3$	0.05	0.07	0.01	6.06
Carbon (C)	8.23	5.30	7.50	
Lost item	16.48	5.19	9.26	4.91

particularly worthwhile to compare the weight percentage values of the major constituents (Ca0, Al_20_3,Mg0, S_102, Fe_20_3, $Ti0_2$ and C) in the following pairs of powders:

(a) Sample I imported powder and coal reject based powder

(b) Sample II imported powder and coal reject based powder

(2) **Thermal conductivity**

The measured conductivities of the imported insulating [powder (samples I and II) and the locally developed powders are presented in Table V. Clearly the values obtained are comparable.

7.0 DISCUSSION OF RESULTS

From tables iv and v, it is seen that the anticipated and actual compositions of the developed insulating powders are reasonably comparable. However the differences between the actual and expected weight percentages of Ca0 and Mg0 indicated that the original assumptions that the line was pure and then the burnt brick was pure Mg0 was wrong.

The actual weight percentage values for Mg0 on table v and 11.64 and 5.95 instead of the corresponding anticipated value of 15 and 10 shown on table IV. From these results, one may find by calculating that the anticipated average value of the magnesia content of the burnt bricks is about 69 wt.%, similarly, it can be deduced from the results that the lime used was only about 82% pure (i.e. its CaO content is 82 wt. %).

Table V shows that the compositions of the sample I imported powder and the coal – reject – based powder are comparable. However, the MgO content is some 100% higher in the developed powder than in the imported one. This is expected to be an advantage for the locally made materials, since MgO is a high quality refractory oxide. It may also be observed that the sample II imported material compares well in composition with the coal – ash – based ladle powder. The effect of the lower silica content in the developed powder may be offset by the slightly higher values of calcium oxide and magnesia. Looking at the compositions displayed on the table, one may conclude that the amounts of coal reject, coal ash, calcium oxide, burnt brick and coal dust used in the development of the powders (See formulae (4) and (6), sections 4.1 and 4.2 respectively, were just right.

The result of the thermal conductivity tests. (table IV) were interesting, because they did not only show that the newly developed powders had comparable thermal insulation properties with the imported ones but also suggested, by the clearly lower thermal conductivity values, that the locally made materials might in fact be superior. It is also worthy of note that the K-value of the coal – ash – based powder (0.12) was lower than that of the coal – reject – based on (0.135). Thus the coal reject and coal ash based powders approximately correspond in composition to imported sample I and II respectively (and also to powder type s I and II respectively, see table I). This suggests that coal – as should be used for the development of type I powders and coal reject for type II powders.

7.1 Raw Material Reserves

A major advantage of the newly developed insulating powders, apart from the obvious benefits of import substitution, lies in the fact that the raw materials were mainly industrial waste materials, which would other wise continue to remain environmental hazards and pollutants

7.1.1 The Nigerian Coal Corporation, Enugu

This is veritable source of coal ash (from coal washery plants) coal dust, and coal rejects. There are some 54 million tones of coal reserve in the Enugu areas with an ash content of some 21.6% heaps and stockpiles of hitherto unwanted coal rejects abound.

7.1.2 The Nigeria Cement company

Nkalagu and the Oji River power station, also in Nigeria are major sources of burt coal which is presently heap rubbish in these Companies.

7.1.3. Delta Steel Company, Ovwian Aladja in Nigeria.

The company imports tones of bricks every year for its Electric Arc furnace vessel lining. These bricks are removed and regarded as waste after some heats and the furnace vessel walls are relined with new bricks. The company is thus a source of burnt bricks which are wastes in the Company.

In addition the company produces lime (CaO) commercially. There is also a lime plant at the Ajaokuta steel company also in Nigeria so that this particular material (which is not necessarily a waste material) will not constitute a problem.

8.0 CONCLUSION

The results of the research effort reported have clearly demonstrated that insulating powders of very high quality can be readily developed from locally available raw materials – mostly industrial coal-based waste materials that nobody at present needs. Preliminary tests on the compounds so far developed are very encouraging. Though the investigation was carried out in Nigeria, the results would be of universal application where these industrial wastes could be sourced.

REFERENCES

1. Delta Steel Newsletter, Vol. II No 7155 on: 0189 – 1707, July 1985

2. Bigger, G.M Cement and Concrete Res. P.I. 493 (1971)

3. Partker, J.W. Proc. Int'l Symp. Chem. of Cement of Cement (London 1952), P. 485.

4. Osborn, E.F. Gee K.H. et al., Bull. Earth Mineral Sci. Expt. Station. Penn. State Univ., P. 85, 80 (1969).

5. Aruja, E: acta Crystallogr. P. 10 337 (1964).

6. Welch J.H. Nature, London. P. 191, 449 (1961)

7. Majumder, H.G. Trans Brit. Ceram. Soc. P. 67, 1 (1964)

8. Midgley, H.G. Trans. Brit. Ceram. Soc. P. 671 (1968)

9. Williams, J. Proc. Brit. Ceram. Soc. Pp 3, 1 (1965)

10. Johnson, D.W. and Schnettler, F.J.J. Amer. Ceram. Soc. P. 53, 44 (1970)

11. Fletcher, J.M. and Hardy, C.J. Chem. and Ind. P. 4, 48 (1968)

12. Cuer, J.P. Elson, J. and Telechner, S.J. Bull. Soc. Chem. Pp 81, 89, 94 (1961)

13. Barry, T.I. Bayliss, R.K. and Lay, L.A.J., Mat. Science, P. 3, 229 (1968)

14. Maziyasni, K.S. Lynch. C.T., and smith, J.S.J and Amer. Ceram. Soc. P. 50, 532 (1967)

15. Waldie, B. Chem. Eng'g No. 259, (March 1972).

16. Thompson, R. "Borides: Their Chemistry and Application", the Royal Institute of Chemistry, (1965)

17. Mathkin, D.I. Science of Ceramics, P. 5, 441 (1970)

17. Obikwelu, D.O.N. Materials in the Service of Man II. Paper Presented at the Nigeria Society of Engineering Meeting, Warri, Nigeria (2005).

18. Obikwelu, D.O.N. Reprocessing of used Refractories. Paper Presented at the Ancillary Industries, Seminar at

19. Delta Steel Company Ltd Ovwian Aladja (1986).

20. Etiese Idorenyin. Markson MSc Project on the Production of Pulverized Coal-rice Husk Briquettes, Department of Mechanical Engineering, University of Nigeria. Nsukka (2007).