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EVALUATION OF FIRE CLAYS FOR IRON AND STEEL REFRACTORIES

Part I. Chemical Characteristics

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An investigation was conducted to search out the possible sources of Mianwali fire-clays that could be used for refractory products in the iron and steel industry. Forty-six samples were collected and studied for their chemical characteristics. The results indicate that the fireclays of Bakwala and Dakpost areas contain high alumina and low iron contents and possess high values of refractoriness. These clays are quite suitable for the production of high quality refractories.

Key words: Fire-clays; Refractory bricks; Steel plant refractories.

INTRODUCTION

Fireclay forms the basis of various refractory products required in the iron and steel industry. It is used as refractory bricks in furnaces, kilns, stoves, runners and ladles of the steel plant where high temperatures are generated. Fireclay refractory bricks are rarely made from a single raw material; the desired properties are generally obtained either by the use of grog or blending of one clay with another.

Russian scientists being the consultants of Pakistan Steel (PS) suggested some standards and specifications for fireclays required for the steel plant refractories. Pakistan Steel, therefore, made an agreement with Pakistan Industrial Development Corporation (PIDC), for the study of the refractory clays. Initially, PIDC experts collected two bulk samples No. (71/ASM/MK/RP-1 and 71/ASM/MK/RP-2) from the refractory clay deposits of Dak Post and Moza Bazar areas respectively near Musakhel, District Mianwali. These samples were sent to the authors for detailed chemical and physical investigations and a preliminary report was submitted to the Soviet consultants of PS who considered the clays suitable for the required purpose. As a result of this, PIDC conducted a detailed geological survey of the Dak Post, Moza Bazar (Bakwala) and Turta areas with a view to exploiting the deposits for the plant. PIDC experts collected 35 channel, 5 lump and 4 representative samples from these deposits.

The fireclay deposits occur in the salt range area near Musakhel, which is situated on the Mianwali-Talagang-Rawalpindi highway at a distance of 13 miles from Mianwali. Dak Post, Bakwala and Turta deposits lie to the north-east and south-east of Musakhel.

The estimated requirement of fireclays for the plant at Bin Qasim is about 55,000 tons per annum [1]. The Dak Post clay reserves have been estimated as 90,000 tons [1] in all. This clay is required for the plant at an annual rate of 15000 tons [1]. Thus the total reserves would be sufficient for 58 years. The Bakwala clay deposits have been estimated as 630,000 tons. [1] They are required at an annual rate of 40,000 tons, and thus they can meet the requirement of the plant for about 16 years.

EXPERIMENTAL

Thirty-five fire clays samples were collected in total from the channels and exploratory adits as per following details[1].

Samples	Locality
1. AM/MB/71/1 to 13	Bakwala (Moza Bazar)
2. AM/DP/71/16 to 25	Dak Post and Chhabil
3. AM/TS/71/14 and 15	Turta (Adit-II)
4. AM/TS/71/26 to 25	Turta and one from Adit-I.

Four representative samples have been collected from the Dak Post, Bakwala and Turta areas. Each representative sample contains equal quantities of the channel/adit samples from the respective deposits. The representative samples have been listed as follows:

Samples	Locality
1. AM/DP/71/RS-1	Dak Post
2. AM/TS/71/RS-2	Turta
3. AM/MB/71/RS-3	Bakwala (Moza Bazar)
4. AM/TS/71/RS-4	Turta Adit-I
5. ASM/MK/71/RP-1	Dak Post area
6. AM/MK/71-RP-2	Moza Bazar area.

In addition to 4 representative samples, the initially collected two bulk sample Nos. ASM/MK/71/RP-1 and RP-2 have also been included in the above list and subjected to detailed evaluation studies.

Chemical analyses were carried out on all the samples. The PCE value determination was restricted to representative and bulk samples only.

The following characteristics have been studied:

1 (a) Chemical properties;
(b) Calculated analysis of fired samples.

2. Mineralogical analysis by:
(a) DTA and (b) X-Ray diffraction;
(c) by calculation.

3 (a) Refractoriness (PCE value);
(b) Calculated refractoriness (PCE value).

1(a) *Ultimate chemical analysis.* All fireclay samples were analysed chemically on dry basis, using the methods for silicate analysis [2]. The following were determined: loss on ignition (I/L) and SiO_2, Al_2O_3, Fe_2O_3, Cao, MgO, Na_2O, K_2O. The results have been presented in the Tables 1 and 2.

(b) *Calculated fired chemical analysis.* Fired chemical analysis was calculated, on the fired basis, from ultimate chemical analysis. The results have been shown in the Table 3.

2. *Mineralogical analysis.* (a) *Differential thermal analysis.* Three samples out of total of six, were prepared by mixing two identical samples into one. RS-1 and RP-1, RS-2 and RS-4 and RS-3 and RP-2 were mixed together. The samples were ground to 100 mesh size, dried at 65° and subjected to DTA determination raising the temperature to 1000°. The differential thermal curves are shown in Fig. 1.

(b) *X-Ray powder diffraction.* Two samples RS-3 and RP-2 were mixed together and were subjected for X-ray diffraction test. The test was carried out by using a 10 cm camera, and nickel filter. A 15 mÅ current and 35 Kv were applied. X-ray pattern has been shown in Fig. 2 and the d values in Table 5.

(c) The mineralogical composition of the six representative samples was calculated from the chemical analysis by following the technique of Koenig [3] and the results have recorded in Table 6.

3(a)*Pyrometric cone equivalent.* (a) Test cones were prepared from the moist clay sample in the shape of a trigonal pyramids with the help of a standard metal mould. The test cones were dried and fired to determine the pyrometric cone equivalent in accordance with the ASTM method [4]. The results have been shown in Table 4.

(b) *Calculated refractories.* (PCE Value). The PCE value has been calculated from the chemical analysis by the application of Schuens formula [5]. The results are included in Table 4.

RESULTS AND DISCUSSION

Initial selection of the refractory clays is usually made on the basis of their chemical composition and refractoriness, although other properties like plasticity, shrinkage, absorption and strength may prove equally important. The chemical composition of the fireclays obtained from the different deposits varies considerably. SiO_2 contents of fire clays of Dakpost area (AM/DP/71/16 to 25) vary from 31.00 to 46.50 % and of Al_2O_3 from 32.0 % to 48.00 %. These clays are of alumino-silicate type or medium type or medium type of fireclays. In the case of Bakwala fire clays (AM/MB/71/1 to 13), the SiO_2 content ranges from 16.00 to 32.2 % and that of Al_2O_3 from 40.00 to 56.6 %. These are aluminous clays i.e. containing high contents of Al_2O_3. The fireclays of the two different localities of Turta area, i.e. AM/TS/71/14 and 15 and AM/TS/71/26 to 35, resem-

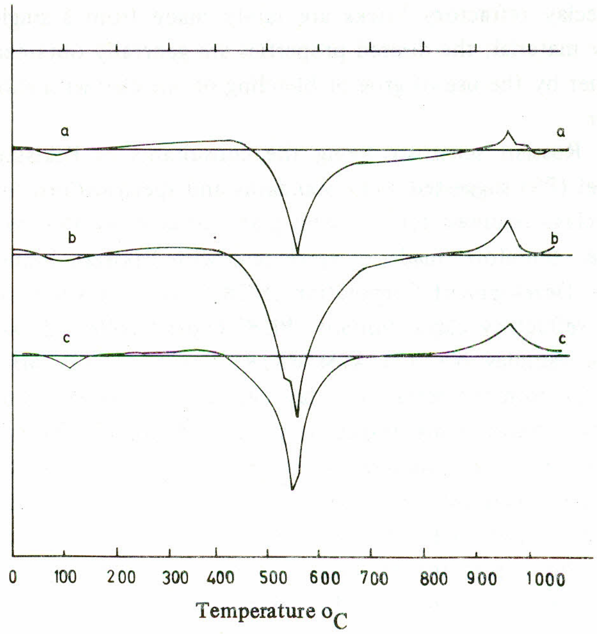

Fig. 1. Differential thermal analysis curves. (a). mix of Rs.-2 and RS-4; (b). mix of RS-3 and RP-2; (c). mix of RS-1 and RP-1.

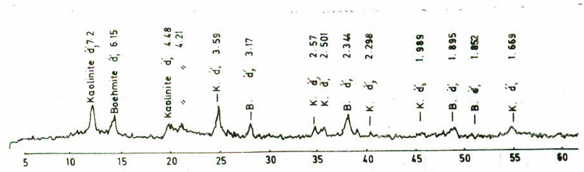

Fig. 2. X-Ray diffraction of RS-2 and RP-2 mix.

Table 1. Ultimate chemical analysis.

Sr. No.	Sample No.	Percentage chemical composition							
		L/I	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
1.	AM/MB/711	7.80	58.20	29.00	1.00	1.40	0.51	1.80	0.2
2.	AM/MB/71/2	6.20	68.00	2.138	0.12	1.39	0.65	1.92	0.25
3.	AM/MB/71/3	15.40	26.60	55.35	0.75	0.55	0.24	1.75	0.04
4.	AM/MB/71/4	14.20	25.80	56.60	0.37	0.70	0.45	1.80	0.04
5.	AM/MB/71/5	25.20	16.00	54.30	0.50	1.40	0.50	2.00	0.05
6.	AM/MB/71/6	14.40	22.00	54.33	0.37	0.73	0.41	2.01	0.045
7.	AM/MB/71/7	14.20	38.20	43.85	0.35	0.75	0.51	1.90	0.03
8.	AM/MB/71/8	12.80	31.30	52.50	0.50	0.70	0.25	1.85	0.06
9.	AM/MB/71/9	13.20	34.20	48.38	0.62	0.75	0.35	2.35	0.09
10.	AM/MB/71/10	17.60	27.00	52.00	0.62	0.68	0.51	1.65	0.02
11.	AM/MB/71/11	14.00	32.00	50.13	0.37	0.35	0.25	2.80	0.10
12.	AM/MB/71/12	13.20	38.00	45.35	0.25	0.72	0.52	1.95	0.06
13.	AM/MB/71/13	13.00	27.60	56.30	0.25	0.70	0.50	1.50	0.01
14.	AM/MB/71/53	15.40	32.40	50.60	0.45	0.84	0.50	2.00	0.09
15.	AM/MB/71/54	14.40	20.00	64.00	0.50	0.35	0.25	2.20	0.08
16.	AM/TS/71/14	13.95	43.00	40.00	0.25	0.70	0.35	1.50	0.30
17.	AM/TS/71/15	12.20	48.80	35.60	0.38	0.70	0.35	2.01	0.35
18.	AM/TS/71/55	7.20	59.70	28.88	0.55	0.70	0.44	2.32	0.49
19.	AM/DP/71/16	11.60	31.00	54.00	0.62	0.70	0.25	1.50	0.15
20.	AM/DP/71/17	13.60	44.00	37.37	0.62	1.72	0.57	1.89	0.22
21.	AM/DP/71/18	11.80	46.30	36.10	1.25	1.41	0.51	2.20	0.31
22.	AM/DP/71/19	14.40	33.20	48.00	1.50	0.35	0.25	·1.91	0.30
23.	AM/DP/71/20	15.00	43.00	39.00	1.25	1.35	0.53	2.51	0.38
24.	AM/DP/71/21	16.80	40.00	38.23	0.87	1.05	0.55	2.17	0.31
25.	AM/DP/71/22	13.00	46.50	36.47	1.53	1.05	0.61	2.09	0.32
26.	AM/DP/71/23	15.00	40.00	31.95	8.55	1.39	0.65	2.28	0.26
27.	AM/DP/71/24	11.80	44.40	39.13	0.87	1.37	0.53	1.88	0.19
28.	AM/DP/71/25	13.60	42.60	39.75	0.75	0.76	0.39	1.75	0.23
29.	AM/DP/71/51	13.00	46.60	38.00	0.65	0.70	0.33	1.70	0.21
30.	AM/TS/71/26	9.00	59.20	26.80	0.50	1.20	0.69	2.39	0.41
31.	AM/TS/71/27	6.80	66.00	21.00	0.75	1.43	0.47	2.50	0.39
32.	AM/TS/71/28	8.00	61.60	25.50	0.50	2.10	0.76	2.13	0.37
33.	AM/TS/71/29	8.40	54.20	32.54	0.86	1.42	0.53	1.71	0.22
34.	AM/TS/71/30	5.00	73.80	17.85	0.25	0.75	0.40	1.53	0.19
35.	AM/TS/71/31	8.00	57.50	28.20	2.00	1.75	0.55	1.67	0.23
36.	AM/TS/71/32	6.00	71.00	18.60	0.50	1.35	0.46	1.39	0.18
37.	AM/TS/71/33	7.20	62.10	25.80	1.50	0.85	0.58	1.75	0.25
38.	AM/TS/71/34	7.00	63.71	23.50	0.75	1.40	0.50	2.69	0.46
39.	AM/TS/71/35	8.40	52.20	35.00	0.75	1.05	0.49	1.59	0.29
40.	AM/TS/71/55	8.60	55.00	33.75	0.45	0.69	0.46	1.85	0.30

ble each other in their chemical composition, with the SiO_2 content ranging from 52.20 to 73.80 %, and the Al_2O_3 content from 17.85 to 35.00 %. These clays are, therefore, silicious i.e. containing high SiO_2 contents.

The impurities present in the clays of the different localities do not vary considerably. The iron content is

Table 2. Chemical analysis of representative samples.

Sr. No.	Sample No.	L/I	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
			Percentage chemical composition						
1.	AM/DP/71(RS-1)	13.4	43.55	38.20	0.85	0.93	0.50	1.75	0.46
2.	AM/TS/71(RS-2)	8.50	60.55	27.4	0.51	0.80	0.49	1.76	0.37
3.	AM/MB/71(RS-3)	14.00	30.70	51.75	0.51	0.70	0.40	1.68	0.05
4.	AM/TS/71(RS-4)	7.50	62.83	25.70	0.52	0.70	0.50	1.77	0.46
5.	ASM/MK/71(RP-1)	13.6	42.21	39.35	1.25	0.90	0.60	1.69	0.40
6.	ASM/MK/71(RP-2)	14.12	30.23	52.22	0.42	0.70	0.50	1.68	0.08

Table 3. Calculated fire chemical analysis.

Sr. No.	Sample No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
		Percentage chemical composition						
1.	AM/DP/71(RS-1)	49.59	44.10	0.97	1.06	0.57	2.23	0.52
2.	AM/TS/71(RS-2)	65.82	29.74	0.55	0.87	0.53	2.36	0.40
3.	AM/MB/71(RS-3)	35.48	59.99	0,59	0.81	0.46	2.02	0.058
4.	AM/TS/71(RS-4)	67.63	27.60	0.56	0.75	0.54	2.18	0.49
5.	ASM/MK/71(RP-1)	48.25	45.27	1.43	1.03	0.69	2.11	0.46
6.	ASM/MK/71(RP-2)	34.91	60.44	0.48	0.81	0.58	2.13	0.09

Table 4. Refractoriness of fireclays.

Sr. No.	Sample No.	Pyrometric cone equivalent: Determined °C	Determined Seger Cone No.	Calculated from chem. composition °C	Calculated Seger Cone No.
1.	AM/DP/71(RS-1)	>1710	>32	1735	34-33
2.	AM/TS/71(RS-2)	1670	30	1665	30-29
3.	AM/MB/71(RS-3)	>1710	>32	1815	37-36
4.	AM/TS/71(RS-4)	1660	30-29	1655	30-29
5.	ASM/MK/71(RP-1)	>1710	>32	1725	33-32
6.	ASM/MK/71(RP-2)	>1710	>32	1810	36-37

less than 1 % in almost all the fireclay samples with the exception of a few, where it goes to 2 % maximum and in one sample i.e. (AM/DP/71/23) it is 8 %. The maximum contents of alkalis present in most of the samples are 2 % and in some they vary upto 3 %. Similarly, the alkaline earths are less than 1.5 % in the majority of the samples and in a minority, these are present upto 2 %.

The chemical compositions of the representative samples as shown in Table 2 are nearly the mean values of the respective samples of the different localities.

Table 5. X-ray diffraction data of RS-3 and RP-2 'd' values.

Kaolinite	Boehmite
7.20	6.15
4.48	3.17
4.21	2.344
3.59	1.895
2.501	1.852
2.298	–
1.989	–
1.669	–

According to the British definitions, B.S.I. 1902, 1952 a fire brick, is a brick that in the fired state consists essentially of alumino-silicates and silica and shows on analysis less then 78 % SiO_2 and less than 38 % Al_2O_3. An aluminous fire brick on the other hand is one that contains Al_2O_3 in the range, 38–45 %.

According to this definition, the calculated chemical analysis on fired basis, as recorded in Table 3, clearly shows that RS-2 and Rs-4 clay samples with 65.72 % and 67.53 % of SiO_2 and 29.64 and 27.50 % of Al_2O_3

Table 6. Calculated mineralogical composition (percent).

Sr. No.	Sample No.	Orthoclase	Albite	Kaolinite	Quartz	Boehmite	Calcite	Magnesite
1.	AM/DP/71(RS-1)	2.71	14.78	67.95	–	9.59	1.65	1.05
2.	AM/TS/71(RS-2)	2.18	14.67	62.08	18.23	–	1.42	1.02
3.	AM/MB/71(RS-3)	0.29	14.19	44.89	–	37.70	1.24	0.84
4.	AM/TS/71(RS-4)	2.71	14.85	58.32	22.01	–	1.24	1.05
5.	ASM/MK/71(RP-1)	2.35	14.32	68.95	–	11.35	1.60	1.26
6.	ASM/MK/71(RP-2)	0.47	14.19	43.49	–	39.39	1.24	1.05

contents, may be considered as alumino-silicate type of fire clays, while RP-1, RS-1, RP-2 and RS-3 with 45.17, 44.00, 60.34 and 59.89 % Al_2O_3 contents respectively, can be suitably taken as aluminous clays. The American Society for Testing materials specifies various grades of fire bricks in terms of refractoriness. For practical purposes, the fusibility or resistance to heat of a ceramic material is generally defined in terms of refractoriness.

According to the above specifications RS-2 and RS-4 fire clays with their PCE values of cone (Seger) 30 and 29, may be regarded as the intermediate duty fire clays. RP-1 and RS-1 having PCE values nearly cone 32, conform to the high heat duty fireclay while RP-2 and RS-3 with PCE of more than cone 32 may be considered at par with super duty fire clay bricks, 50 and 60 % alumina bricks on the basis of their high Al_2O_3 contents.

Similarly, if the chemical composition and refractoriness values of the local fireclays are compared with those of the Russian specifications [7], it can be observed that RS-1, RS-3, RP-1 and RP-2 clays by virtue of their high Al_2O_3, low iron contents and high refractoriness values are superior to the plastic and flint clays required by them. Thus, local clays can prove better in actual practice. RS-2 and RS-4 clay values, on the contrary are lower than their specifications and therefore, they cannot be recommended for this purpose. Chesters and Howie [8] studied the action of blast furnace slags on six fire clay bricks which have been found to give good service in the blast furnace lining. They have also summerized the properties of the principal casting pit refractories [8] (i.e. runner bricks, rod covers, nozzle, stoppers and mould top bricks etc.), which were in use in the United Steel Companies (UK). Their experiments and observations enable one to gain a fair idea of the types of materials considered most desirable for iron and steel refractories. By comparing the chemical composition and refractoriness value of our clays with those of the above cited fire bricks, it can be ascertained that our four fire clays i.e. RP-1, R-2, RS-1 and RS-3 may prove better and give good results in the works, while RS-2 and RS-4, clays may behave slightly inferior to these bricks. The free silica contents present in the casting pit refractories may be of some importance, since silica tends to be reduced by manganese [9].

The bricks, therefore, required in iron and steel works should be more refractory and able to show greatest tolerance for FeO and MnO.

In addition to the above, the presence of free silica also increases the susceptibility to attack by basic slags. In modern industrial practice, a few slags are on the acidic side, and so the range of utility of high silica fire clays (i.e. RS-2 and RS-4) is limited to these cases only where the slag attack is negligible, e.g. in chimneys, flues and outer furnace linings. Thus RP-1, RS-1, RP-2 and RS-3 clays will give better performance under such conditions than RS-2 and RS-4.

The behaviour of a clay at high temperature is entirely dependent on the minerals present in it. The mineralogical composition data is shown in Table 6, and DTA curves in Fig. 1. According to Mackenzie [10] gibbsite and boehmite minerals give a single endothermic peak between 260-380° and 510-580° respectively in their DTA curves. The endothermic peak at 530-560° and a smaller exothermic peak at 920-960° is characterized by kaolinite mineral. Since the endothermic reactions for both boehmite and kaolinite take place in the same range of temperature, sometimes a single peak represents the presence of both minerals while in some others two separate and distinct peaks may indicate the respective minerals. The occurence of a sharp endothermic peak between 540-560° and a small exothermic peak between 950-960° in sample No. RS-1 and RP-1 show the presence of kaolinite and boehmite. The endothermic peaks at 540 and 560 in sample RS-3 and RP-2 clearly indicate the presence of boehmite and kaolinite minerals respectively.

X-Ray diffraction results of samples No. RS-3 and RP-2 are presented in Table 5 and Fig. 2. The 'd' values obtained are compared with the standard 'd' values of kaolinite and boehmite. It may be observed from Table 5 and the X-ray diffraction pattern of Fig. 2 that a major amount of the mineral is kaolinite while boehmite is also present in association with it. The intensity of lines 7.20, 4.48, 4.21, 3.59, 2.501 etc. shows the presence of kaolinite while that of lines 6.15, 3.17, 1.852 etc. indicate boehmite.

The mineralogical composition data in Table 6 show evidently the presence of free silica (19.23 and 22 %) as an impurity in samples RS-2 and RS-4, while boehmite is associated with other clays. In general the higher the alumina content in a fireclay, the greater is the refractoriness. This general rule is also applicable here. As the percentage of boehmite increases in these clays the refractoriness goes on increasing and it decreases as the silica content increases. Thus the low PCE values of RS-2 and RS-4 may be attributed to the presence of low Al_2O_3 and high silica contents in these clays.

Bricks made of fire clays with high alumina contents have higher spalling resistance than the average fireclay brick [11] and possess greater resistance to slag attack [11]. Thus the refractories made of RS-3 and RP-2 fire clays may prove very resistant to severe slagging conditions and temperature fluctuations and that of RS-1 and RP-1 for moderate conditions.

Other noticeable impurities present in the clays are alkalis which amount to 2 %. Alkalis act as fluxes and melt to form a liquid with Al_2O_3 and SiO_2 at lower temperature and thus cause vitrification problem by reducing the porosity of the products. The action of the fluxes depends upon the firing temperature, the form in which they are present and the grain size of the minerals containing them. The alkali present in these fireclays are in the form of feldspar (or mica) and so they do not readily react unless the minerals are finely divided.

CONCLUSION

From the foregoing discussion it appears that the Dak Post area fire clays containing Al_2O_3 32–48 % can be suitably used for manufacturing the aluminous or high heat duty fire bricks.

The Bakwala fire clays with 40–56.6 % Al_2O_3 may be used for the production of super duty, and 50 or 60 % alumina-diaspar bricks either separately or by blending with clays of Dakpost area. Its total reserves being sufficient to run the installed iron and Steel Plant for 16 years, the search to locate new deposits of similar or better quality of fire clays may be continued.

Turta area clays are ordinary type of fire clays with high silica contents. Therefore, these can be used in those refractory products where the slag attack is not an important factor.

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