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A Preliminary Study of Furnace Materials from Shuiquangou Iron Smelting Site of Liao and Jin Period in Beijing

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Microstructure, chemical composition, physical property and high temperature process of furnace materials from Shuiquangou site were analyzed in order to promote an exploratory scientific study on cast iron smelting furnace materials in ancient China. The results showed that raw materials were locally collected and gone through a screened process; there were at least two productions of furnace lining which used in different parts of the furnace. Furnace materials can provide enough Na_2O, Al_2O_3, and SiO_2 into slags. The refractoriness of them were about 1 200–1 300°C, and the smelting temperature was among 1 300–1 500°C.

KEY WORDS: furnace material; furnace lining; blast furnace; cast iron; refractory material; Shuiquangou site.

1. Introduction

In the last few decades, about 154 ancient iron smelting furnaces were found in 93 iron smelting sites throughout China. Chinese scholars had focused on the research of iron object, slag, furnace design, blast equipment and iron industry organization for a long time. And, in 1970s, scientific research methods have been involved into the study. However, furnace material was not taken very seriously in the past.

Furnace material plays a very important role in metallurgical processing, such as keeping the furnace structure stability, providing silicate material into slag and maintaining the high temperature in the furnace. Though ancient furnaces have been found throughout China, only a few of them have been studied in detail. Qingyun Zhao and Rubin Han tested the chemical composition and melting point of samples from Teishenggou site, Gongyi city, Henan province.[1)] The same experiments were also carried out in Guxing[2,3)] and Wafangzhuang[4)] sites in Henan province.

References on research furnace material were mostly from ancient high-tech ceramic or refractory material studies. K. D. Kingery[5,6)] did a very early research on observing microstructure of cooper smelting furnace lining from Rothenberg site by using SEM. After that, many cooper smelting furnace linings, crucibles and tuyeres were analyzed by R. F. Tylecote,[7)] I. C. Freestone,[8,9)] M. S. Tite,[8,10)] Thilo Rehren,[11–13)] Yanxiang Li,[14)] Marcos Martinón-Torres,[15–19)] Lesley Frame,[20)] Anno Hein,[21)] C. P. Thornton,[22)] Pengfei Xie[23)] and Wenli Zhou.[24)] The methods they used included mineralogical, chemical and phase analysis, as well as re-firing experiment. Their researches basically believed that the ancient refractory materials were not fit with modern criterion, the refractoriness were mostly lower than 1 200–1 300°C. The source of raw materials, the different features among different materials and sociotechnical system were also discussed. Among them, Lesley Frame's work was an exploration of microstructure and thermal analysis by using point counting and DTA methods.[20)]

Past research provide some knowledge about iron smelting furnace material and give us experiences on analyzing this type of material. However, there are still many questions need to be answered, such as what are they (material features)? How people made them (raw materials and technology)? Are there any differences between different types, regions and periods? More importantly, why people made them? Are they real refractory materials? And what can we know about smelting technology when analyzing them? ... In order to achieve a better understanding, a systematical study on furnace materials excavated from iron smelting sites throughout China were promoted, and Shuiquangou site perfectly provided a chance to carry out an exploratory study.

2. Shuiquangou Iron Smelting Site and Samples

Shuiquangou site is located in Yanqing County, some 45 kms from Beijing. It was found in 2005 and invested by University of Science and Technology Beijing (USTB) and Peking University (PKU) from 2008 to 2011, after that, two times of excavations were carried out by Beijing Institute of Cultural Relics, USTB and PKU. The site is consists of five regions, No. 1, No. 2, No. 3 and No. 5 regions were iron smelting areas, No. 4 region was considered as living area,

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No. 1 and No. 4 regions were partly excavated. Location map is shown in **Fig. 1**.

There are four furnaces found in No. 1 region and one in No. 2 region. Furnaces in No. 1 region were cleaned out, and slag, ore, carbon, as well as furnace materials were unearthed. Archaeological date and AMS-^{14}C test showed that the site and furnaces were among Liao and Jin period (AD 907 – AD 1234). Before this work, Wei Kong analyzed several slag samples,[25] and Wei Wei finished a 3D laser scanning work.[26]

The No. 3 furnace in No. 1 region is considered as the best preserved ancient furnace in China by far. The top half of it was collapsed and many furnace materials were fallen down on the bottom, while the lower half preserved very well and covered by adhering slag. From the inner layer to the out layer of the furnace wall are adhering slag, furnace lining, stone wall with medium-sized stones (≤30 cm) and stone wall with large-sized stones (≥30 cm). The stones were cut carefully into square-shaped and were jointed rigorously with not many cracks can be seen, they are structural and load-bearing components of the furnace. Side-opening (furnace door) was destroyed with only a few existed on the edge. Furnace lining, side-opening material and jointing material were unshaped, while tapping channel lining were shaped. Samples were directly collected in excavation, the detailed information is shown in **Table 1** and **Fig. 2**.

3. Experiments

3.1. Microstructure Analysis

Samples were cut from furnace materials and made into thin sections which has been ground and polished to a thickness of 30 microns in the Laboratory of Orogenic Belts and Crustal Evolution of PKU. Then petrographic analyses were carried out with an Olympus polarizing microscope in the Archaeometallurgy Laboratory of PKU. Minerals were identified using both plane and cross-polarized light.

Point counting method[27] was promoted on each thin section to obtain their microstructural information on rocks, minerals, clay matrix and voids. Point counting procedure in this study was divided into two stages: first, the number of big rocks, big purely minerals and big voids were counted under 10×0.25 magnification; second, the number of clay, small purely minerals and small voids were counted in the picture which was taken under 10×0.25 magnification.

Besides, samples were also cut from slags, after being grounded and polished, they were observed and photographed with a Leica DM4000M metalloscope at the Archaeometallurgy Laboratory of PKU and Carl Zeiss EVO18 SEM at the School of Materials Science and Engineering of USTB.

3.2. Compositional Analysis

3.2.1. Chemical Compositional Analysis

The bulk compositions of furnace materials and adhering slags were collected through wet chemical analysis at the Chemical Analysis Center of USTB. The composition of SiO_2, Al_2O_3, Na_2O, MgO, K_2O, CaO and Fe_2O_3 of furnace materials were mainly focused while FeO replaced Fe_2O_3 when analyzing adhering slags.

Slags were analyzed by using a Carl Zeiss EVO18 SEM with EDAX Genesis 2000 XMS in the School of Materials Science and Engineering of USTB. The excitation voltage was 20 kV, the collecting time is 75 seconds. Slag samples were spot scanned at bulk and matrix conditions for three times on each; points chosen for measurement were special phases.

3.2.2. X-Ray Diffraction

X-Ray Diffraction (XRD) was used to identify the mineral components of the furnace materials and to certify the results of microstructure observation. Meanwhile, it shows the mineral types in adhering slags, to understand the temperature it processed when clay and quartz transferred into other minerals.

All XRD was performed at Micro Structure Analytical Laboratory of PKU, samples were analyzed using a Dmax 12 kW XRD unit at settings of 1° convergence slit, 1° scatter slit, 0.3 mm receiving slit, 40 kV and 100 mA. 2θ values were set at 27°C, and the sampling interval was set at 0.02°. The scan speed was 8°/min for the initial scans and 2° for the slower scans. The samples were prepared in powdered form and dry-mounted on a glass slide.

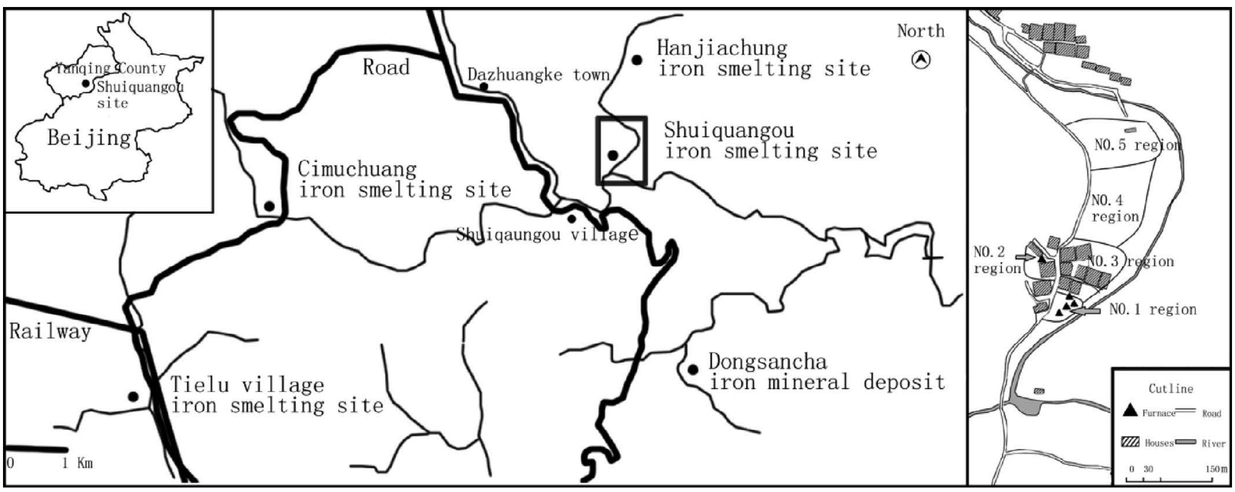

Fig. 1. Map of Shuiquangou iron smelting site.

Table 1. Samples and their corresponding experiments.

Type	Sample No.	Description and location	Experiments
Furnace lining (FL)	11Y3:3	Yellow, with a thin layer of adhering slag, top half	TSA, WCA, XRD, DTA
	11Y3:8	Yellow, top half	TSA, WCA, XRD, PPA, DTA
	11Y3:9-1	Red, top half, nearby rock	TSA, WCA, XRD, PPA, DTA
	11Y3:9-2	Yellow	TSA, WCA, XRD, PPA, DTA
	11Y3:9-3	Black, nearby adhering slag	TSA, WCA, XRD, PPA, DTA
	11Y3:10	Yellow, connected with a piece of rock, top half	TSA
	11Y3:12	Red, top half	TSA
	12Y3:7	Black, bottom	TSA, WCA, XRD, PPA, DTA
Tapping channel lining (TL)	12Y3:8	Black, block shaped	TSA, WCA, XRD, DTA
	12Y3:9-1	A white thin coat with spots of iron corrosion	TSA, WCA, XRD, DTA
	12Y3:9-2	Red, block shaped	TSA, WCA, XRD, DTA
Side-opening material (FD)	11Y3:11	Yellow matrix with slags, the slags were scattered in the matrix, and disconnected with each other	TSA, WCA, XRD, DTA
Rock (R)	12Y3:2	White, top half	TSA
	11Y3:10-r	White, top half	TSA
Adhering slag (AS)	12Y3:1	Black, glassy, middle part	XRD, SEM-EDS
	12Y3:3	Black, glassy, lower part	WCA, XRD, SEM-EDS
	12Y3:4	Black, glassy, lower part	SEM-EDS
	12Y3:5	Black, glassy, bottom	SEM-EDS
	12Y3:6	Black, glassy, bottom	WCA, XRD, SEM-EDS
Glassy slag (GS)		Tapping slag, black, glassy, 11Y3:2, 11Y3:5-1, 11Y3:5-2, SEM-EDS	

TSA- Thin section analysis; WCA- Wet chemical analysis; PPA- Physical property analysis.

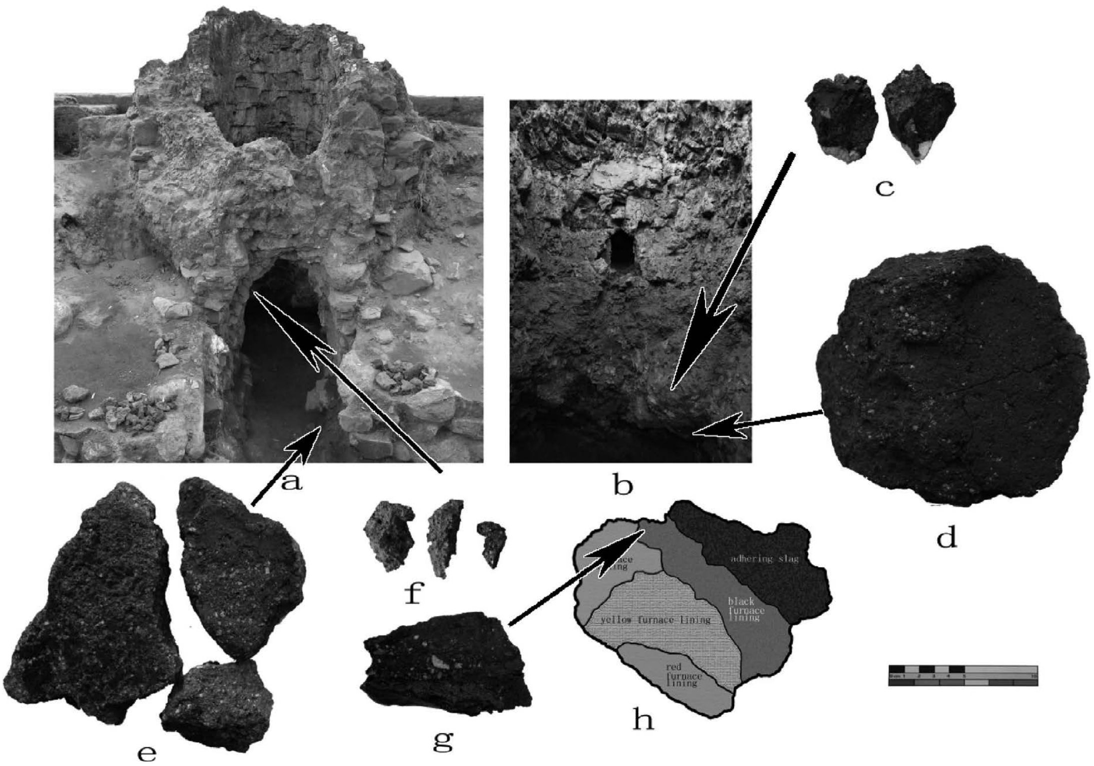

Fig. 2. No. 3 furnace and samples (a- furnace; b- inner wall and blast hole; c- 12Y3:6, adhering slag on the lower part; d- 12Y3:7, furnace lining on the bottom; e- 12Y3:9, tapping channel lining; f- 11Y3:11, side-opening materials; g & h- 11Y3:9, a big furnace lining with layers in different colors, from red to black are furnace lining and adhering slag).

3.3. Physical Property Analysis

Physical properties were not concerned in the previous studies. This research was plan to test some items of physical properties using modern methods, including volume density, apparent porosity, true density, water absorption, refractoriness, refractoriness under load (R-U-L), Hot Modulus of Rupture (HMOR), thermal shock resistance and slag resistance. However, ancient materials were so instable that most test programs were not appropriate to use. Only volume density, apparent porosity, true density and water absorption were analyzed at the Laboratory of Refractory Materials, China Building Materials Test Center.

3.4. Different Thermal Analysis

Thermal analysis was aim to know the firing temperature that the furnace materials has been processed as well as to understand the highest temperature that these materials are capable of sustaining.[20] DTA can well establish the endothermic and exothermic events occurred in the heated process, it's a useful method in determining the original firing temperature of a ceramic.[20] Sintering temperature, vitrified temperature, softening temperature, melting temperature and final temperature could be known when analyzing the DTA curve. Meanwhile, by comparing different curves of different parts' materials, the whole firing conditions of a furnace could be understood.

DTA analysis was taken at the State Key Laboratory of New Ceramics & Fine Processing of Tsinghua University, the samples were heated from 0°C to 1 400°C at a rate of 10°C per minute under a common air condition atmo-

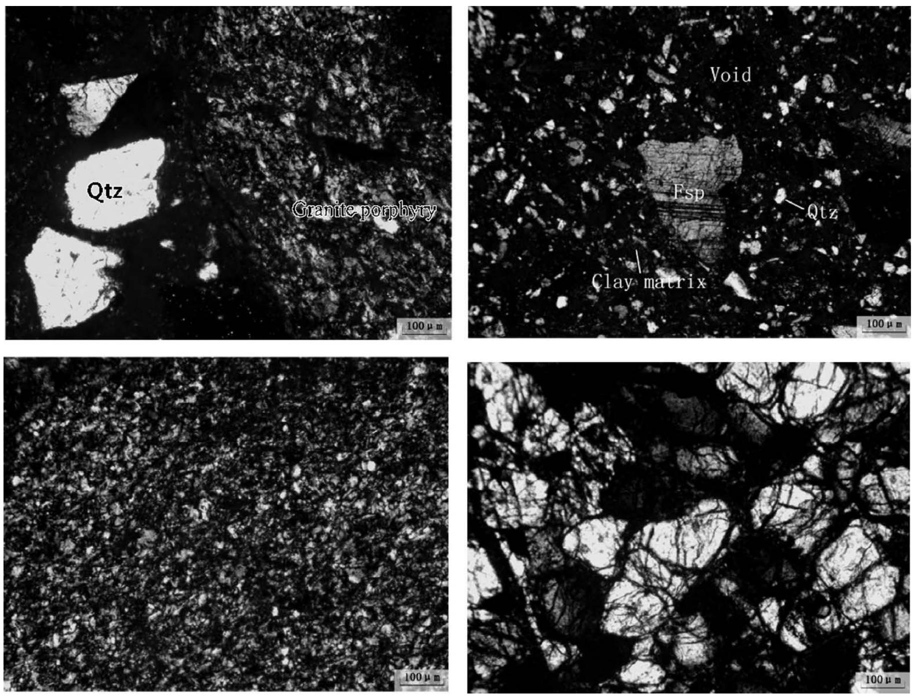

Fig. 3. Microstructure of furnace linings (the above two pictures) and stones.

Table 2. XRD results of samples (wt:%).

Number	Type	Quartz	Plagioclase feldspar	Amphibole	Mullite	Cristobalite	Tridymite	Magnetite	Others
11Y3:3	FL	22	–	–	51	27	–	–	
11Y3:8	FL	26	69	1	–	–	–	–	Muscovite:4
11Y3:9-1	FL	76	24	–	–	–	–	–	
11Y3:9-2	FL	63	34	–	–	–	–	–	Hematite:4
11Y3:9-3	FL	45	41	6	–	–	–	2	Dolomite:6
11Y3:11	FL	8	2	5	60	19	6	–	
12Y3:7	FL	30	69	–	–	1	–	–	
12Y3:8	TL	29	68	1	–	–	–	1	Muscovite:1
12Y3:9-1	TL	19	43	3	–	–	–	2	Analcime:32
12Y3:9-2	TL	25	70	1	–	–	–	–	Muscovite:4
12Y3:1	AS	4	–	–	52	14	–	13	Hematite:3
12Y3:3	AS	17	5	–	39	20	13	–	Hematite:6
12Y3:6	AS	3	–	–	57	15	26	–	

sphere.

4. Results

4.1. Mineralolgical Phases

Furnace linings were all consist of clay matrix and inclusions. Clay was binder between inclusions; grains which were larger than 1 000 μm were all rocks (mostly quartzite and granite), fines were small quartz and plagioclase feldspar which were mostly smaller than 1 000 μm. Stones which were building materials of the furnace were granite and granite porphyry.

Meanwhile, XRD results also claimed that the mineralogical phases were mostly purely quartz and plagioclase feldspar though some were transferred into other phases during high temperature process. Some photos of mineral phases are shown in **Fig. 3**. The XRD result can be found in **Table 2**.

4.2. Point Counting Result

Fifteen thin sections were made, however only 10 can be used on point counting method, for some were seriously glassy. Point counting results are shown in **Table 3**.

4.3. Buik Composition

Bulk compositions are shown in **Table 4**. The results of

Table 3. Point counting results of thin sections.

Numer	Type	Quartzite %	Granite %	Quartz %	Matrix %	Voids %	Plagioclase Feldspar %	Others %
11Y3:3	FL	37.1	17.4	13.8	6.9	23.9	0.9	–
11Y3:8	FL	31.9	14.7	18.0	16.4	18.0	0.5	0.5
11Y3:9-1	FL	24.1	10.9	20.8	24.1	17.2	2.9	–
11Y3:9-2	FL	26.4	11.5	18.6	23.6	14.3	5.6	–
11Y3:9-3	FL	15.4	7.4	21.8	14.0	33.5	7.0	0.9
11Y3:10	FL	25.9	11.1	13.2	22.7	10.1	11.3	5.7
11Y3:12	FL	27.8	13.8	18.3	21.2	12.4	6.5	–
12Y3:7	FL	15.8	8.3	22.1	17.5	29.7	6.6	–
12Y3:8	TL	16.4	11.0	13.7	20.3	33.7	4.9	–
12Y3:9-2	TL	17.9	11.4	17.5	18.8	30.1	3.9	0.4

Table 4. Bulk composition of samples (wt:%).

Number	Type	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	FeO
11Y3:3	FL	0.78	0.31	32.2	56.5	1.80	0.27	2.07	–
11Y3:8	FL	4.15	1.19	15.6	58.6	3.61	1.39	5.31	–
11Y3:9	FL	2.24	1.41	17.8	60.3	2.91	0.96	4.84	–
11Y3:11	FL	0.85	0.61	35.5	52.1	1.32	0.39	3.5	–
12Y3:7	FL	4.05	1.19	13.2	61.6	4.37	1.58	4.07	–
12Y3:8	TL	4.35	1.16	13.4	62.9	5.46	1.66	3.88	–
12Y3:9-1	TL	3.46	2.08	15.5	52.3	6.38	1.49	6.01	–
12Y3:9-2	TL	4.42	1.34	18.6	57.7	3.78	1.81	3.43	–
12Y3:1	AS	0.2	0.7	25.4	54.9	14.4	0.5	–	2.7
12Y3:3-WCA	AS	1.03	1.28	22.1	51.8	9.33	1.13	–	3.36
12Y3:3-EDS	AS	1.4	2.1	26.2	56.4	9.9	1.9	–	1.8
12Y3:4	AS	0.2	0.9	31.8	55.2	7.1	0.3	–	2.8
12Y3:5	AS	0.5	2.2	20.7	67.2	4.3	1.7	–	3.3
12Y3:5-matrix	GS	0.7	5.4	10.8	54.8	8.0	15.5	–	4.0
12Y3:6-WCA	AS	0.44	0.43	30.6	56.8	2.29	0.43	–	3.98
12Y3:6-EDS	AS	0.3	1.1	31.6	57.8	2.6	1.3	–	3.8
11Y3:2	GS	3.6	1.5	21.1	61.1	5.2	3.1	–	3.9
11Y3:5-1	GS	1.6	15.3	14.5	49.6	3.3	7.1	–	6.3
11Y3:5-2	GS	0.6	9.2	16.0	52.6	3.2	10.4	–	5.4
Previous research	GS	–	8.2	6.4	55.5	3.3	15.7	–	9.9

wet chemical analysis and SEM-EDS of two adhering slags were very close demonstrated that the data were available to compare.

4.4. Physical Property

Three large furnace linings were gone through a physical property analyze, this part of analysis could be used to promote a comparative study of furnace materials found in other regions. Results of physical property tests are shown in **Table 5**.

4.5. DTA Result

Before DTA test, samples were fired in resistance furnace to observe when it begin soften, then the limited temperature in DTA test was determined. The result of re-fining experiment showed that most samples were soften around 1 300°C, so the highest limited temperature were set around 1 350–1 400°C in this study. DTA curves can be seen in **Fig. 4**.

5. Discussion

(1) Granite and granite porphyry are very typical rocks in this region,[28] strongly illustrated that raw material of stones were locally collected. And, material features of furnace linings are conform to the characteristics of local soil which is consists of granite, granite porphyry, quartzite, quartz and plagioclase feldspar, as well as clay bodies, suggested that raw material of furnace linings were also locally produced. Meanwhile, there were not many differences between raw materials of furnace linings, tapping channel linings, jointing materials and the matrix of side-opening materials.

(2) Large pieces of rocks were very common in these materials showed that raw materials were not treated strictly like the raw materials on making pottery or casting mold. The sizes of large rocks were mostly smaller than 3 mm demonstrated that raw materials of soil were only screened through 3 mm sieve.

However, since the slags in the side-opening material are scattered in the clay, and disconnected with each other, they might be tempered rather than intruded. Moreover, the bottom furnace lining and tapping channel lining were found been shaped.

(3) By comparing constitutes of inclusions, voids, rocks and clay matrix of furnace linings, we can see that 11Y3:9-1, 11Y3:9-2, 11Y3:10 and 11Y3:12 are always gathered together, while 11Y3:9-3, 12Y3:7, 12Y3:8 and 12Y3:9 are huddled, see **Figs. 5–7**.

Table 5. Results of physical property tests.

Number	Type	Volume density	True density	Apparent porosity	Water absorption
12Y3:7	FL	1.88 g/cm^3	2.640 g/cm^3	28.5%	15.1%
11Y3:8	FL	1.91 g/cm^3	2.640 g/cm^3	27.0%	14.1%
11Y3:9	FL	1.60 g/cm^3	2.612 g/cm^3	39.5%	24.8%

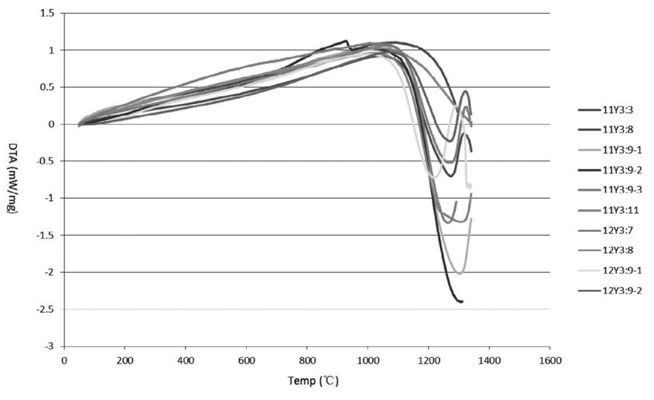

Fig. 4. DTA curves.

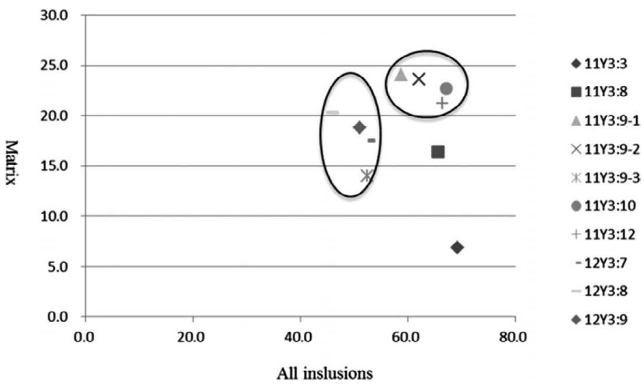

Fig. 5. Bivariant plot of thin section mineralogy, all inclusions vs. matrix.

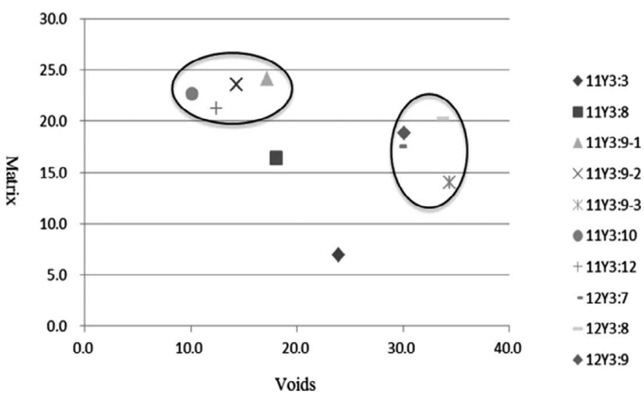

Fig. 6. Bivariant plot of thin section mineralogy, voids vs. matrix.

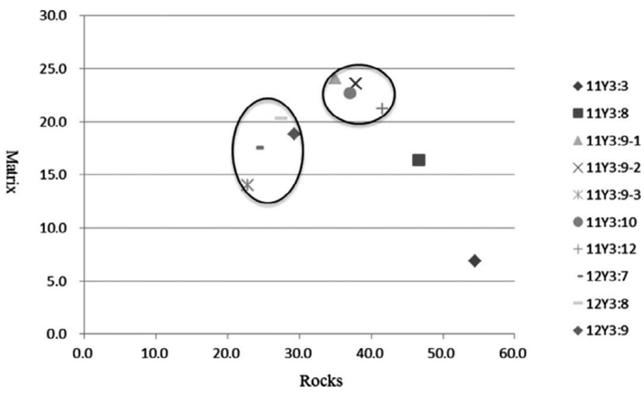

Fig. 7. Bivariant plot of thin section mineralogy, rocks vs. matrix.

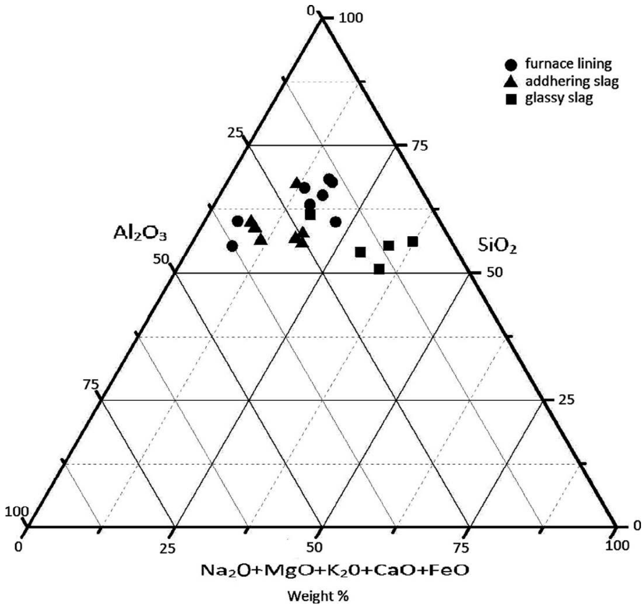

Fig. 8. Scatter diagram of bulk composition of furnace linings, adhering slags and glassy slags.

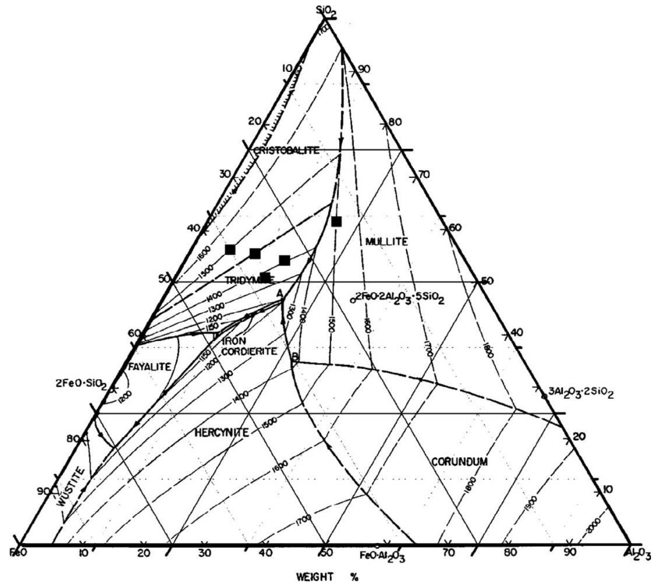

Fig. 9. Smelting temperature was among 1 300–1 500°C through ternary diagram observation.

Table 6. Ratios of each chemical composition between slags and furnace linings.

Type	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO
AS-average	0.6%	1.3%	27.7%	58.8%	7.3%	1.1%
GS-average	1.3%	8.0%	14.0%	55.6%	4.7%	10.5%
FL-average	3.3%	1.3%	22.2%	63.3%	4.1%	1.3%
AS/FL	0.2	1.0	1.2	0.9	1.8	0.8
GS/FL	0.4	6.3	0.6	0.9	1.1	8.0

It seemed that raw materials were processed into two different productions. The production which had more voids, fewer inclusions and rocks was used to make the inner and the bottom of furnace lining, as well as tapping channel lining.

(4) From the scatter diagram of bulk composition (see **Fig. 8**), it can observed that adhering slags always have the same composition as furnace linings, while glassy slags don't. It may because adhering slags were mostly from furnace linings. However, glassy slags have other sources, such as ores and fluxes.

By comparing ratios of contents in slags and furnace linings (see **Table 6**), the result showed that furnace lining can provide enough Na_2O, Al_2O_3 and SiO_2 into slag, which means furnace lining is the main source of silica material when smelting. On the other hand, K_2O, MgO and CaO need other origins, and it may support the idea that they add dolomite when smelting, and K_2O was mostly from carbon ash.

(5) The furnace lining was not only provided silica material but also refractory material. However, they did not fit the modern standard of refractory material for its refractories was much lower than 1 580°C. From the result of DTA analysis, the curves showed that all samples experienced a melting process between 1 200°C and 1 300°C, it illustrated that the refractoriness may around that. The functions of furnace materials were not only focused on the temperature they could be sustained but also provide silica, so it's truly that they were born as "sacrificial furnace lining".

(6) The smelting temperature can be speculated by the results of DTA analysis and ternary diagram observation. There are many high temperature phases (like mullite, cristobalite and phosphorus quartz) which transferred from clay and quartz were found in the samples. DTA curves showed that the firing temperature of them may overlapped with melting temperature which mostly around 1 200–1 300°C. However, the ternary diagram analysis demonstrated that the smelting temperature should be higher than that, approximately 1 300–1 500°C (see **Fig. 9**).

6. Conclusion

The scientific study of furnace materials excavated from Shuiquangou iron smelting site is an exploratory study; microstructure, chemical composition, physical property as well as high temperature process were tested. The results showed that raw materials were locally collected and processed a simple screening technique; slags were tempered into soil to make side-opening material, and the bottom furnace lining and tapping channel lining were shaped. It was found that furnace linings on the inner layer and the bottom of the furnace were made from the same material as tapping channel lining. Furnace materials can provide enough silica material when smelting, the refractoriness of furnace lining was about 1 200–1 300°C. The smelting temperature was at least higher than that. Moreover, the results need to be compared with furnace materials found in other sites to gain deeper insight on the history of ancient cast iron smelting furnace materials.

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