INFLUENCE OF ALKALIS ON MECHANICAL PROPERTIES OF LUMPY IRON CARRIERS DURING REDUCTION

Anton PICHLER[a], J.L. SCHENK[a], M.B. HANEL[a], H. MALI[b], F. HAUZENBERGER[c], C. THALER[d], H. STOCKER[e]

[a] *Chair of Ferrous Metallurgy, Montanuniversitaet Leoben, Leoben, Austria, EU*
[b] *Chair of Geology and Economic Geology, Montanuniversitaet Leoben, Austria, EU*
[c] *Siemens VAI Metals Technologies GmbH, Linz, Austria, EU*
[d] *voestalpine Stahl GmbH, Linz, Austria, EU*
[e] *voestalpine Stahl Donawitz GmbH, Leoben, Austria, EU*

Abstract

Alkaline metals like sodium and potassium are generally known as unwanted elements in ironmaking processes. Beside the negative effects on refractory and coke consumption, alkalis have a negative influence on the mechanical stability of the feed material. Previous research work has shown the correlation between alkali content and the destruction of iron ore pellets. To investigate the effects of sodium and potassium on all kinds of lumpy iron carriers, reduction and tumbling tests were executed under various experimental conditions. Limonitic and hematitic raw ores and pellets were treated with alkali bearing aqueous solutions to soak the particles. Investigations by SEM and microprobe showed different alkali adsorption properties of mineralogical phases of the feed materials. Elevated contents of sodium and potassium were detected in limonite, gangue and glass phases after soaking. The soaked materials were reduced in a vertical retort furnace according to ISO standards and at conditions comparable to those of industrial processes. After tumbling the reduced material the grain size distribution was determined. A significant effect of alkalis on disintegration, degradation and sticking behaviour of lumpy iron carriers during reduction could be demonstrated. Additionally the different impacts of sodium and potassium were quantified. Due to investigations on different types of lump ore and pellets, various effects of sodium and potassium on mechanical properties were quantified.

Keywords: ironmaking, alkalis, reduction, sticking, degradation, lump ore, pellets;

1. INTRODUCTION

From experience in industrial applications, we know that alkali metals as sodium and potassium are disadvantageous elements in ironmaking processes. The main issues concern macroscopic effects like the formation of scaffolds by gaseous and liquid alkaline compounds or the general increase of fines due to increased values of alkali metals in the reactor [1]. However, these effects are mainly caused by microscopic reactions. Previous research primarily focused on iron ore pellets and coke. Investigations on alkali-treated pellets show swelling during reduction [1,2]. Of course these changes in volume lead to degradation of the particle and to higher values of fines. In addition, tests with alkali-treated coke lead to higher amounts of dust in comparison with untreated material [3]. It is also necessary to evaluate other input materials for ironmaking processes, e.g. different types of lump ore. A methodology was developed to characterize lumpy iron carriers and their behaviour under the influence of alkali metals, which is described in this paper. Variable input material for ironmaking like hematitic lump ore, limonitic lump ore and two brands of pellets were soaked with sodium or potassium. The separation between these two alkali metals was essential to obtain clear information about the specific effects; especially for industrial applications a clear partition of the different alkali metals is desirable. Reduction tests were performed in both standardized and modified near industrial process conditions for non-soaked and soaked material. Afterwards sieve analyses and tumbling tests showed a process near picture of mechanical load and its effects on particle strength. The parameters for the experiments and the results with lump ore and pellets are shown in the following.

2. EXPERIMENTAL SETUP

The reduction of the lumpy iron carrier is carried out in a vertical lab scale reduction retort. The experimental setup including the main technical data is shown in **Fig. 1**. The process gas for the reduction tests is supplied by a gas supply unit. For the required testing procedures specific reducing gas compositions are produced by mixing pure components like CO, CO_2, H_2 and N_2. The core of the plant is a retort with 75 mm in diameter, and is heated by an inductive heating system. The reducing agent enters the material bed from the bottom side. The temperature is measured by a thermocouple in the fixed bed. The retort hangs on a weighing cell, which measures the removal of oxygen of the iron carrier by mass loss. Based on this information the change in the reduction degree is calculated by the ratio of removed oxygen during reduction to the total content of oxygen originally bound to iron. The process control system of the plant allows for the tests to be executed with defined time profiles for the sample temperature and reducing gas composition. The main test parameters are listed in **Table 1** [4,5]. The mechanical properties are determined in a tumbling system (see **Fig. 2**). The reduced material is then fed into the rotating chamber and drum for 30 minutes with a rotation speed of 30 rpm. The separation of the different grain size fractions occurs by sieving, thereby providing the mass for the disintegration and the abrasion tendency calculations in **Table 2**. The initial mass prior to tumbling is m_0- m_1 stands for the mass portions > 6.3 mm in g after tumbling- m_2 stands for the mass portions < 0.5 mm in g after tumbling.

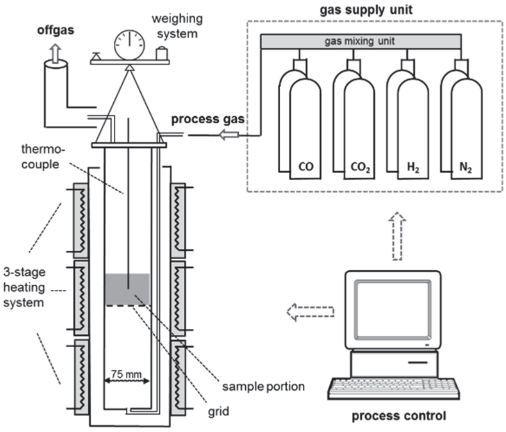

Fig. 1 Plant layout of the testing equipment including gas supply system [4]

Table 1 Testing parameters for reduction tests including calculation and description of characteristic values [4]

Sample portion	500	[g]
Max. testing temperature	950	[°C]
Size fraction of input material	10 - 12.5	[mm]
Reduction degree	$RD = \left(\frac{O_{removed}}{O_{tot}}\right) \cdot 100$	[%]
Time to achieve 80 % of reduction	RD_{80}	[min]

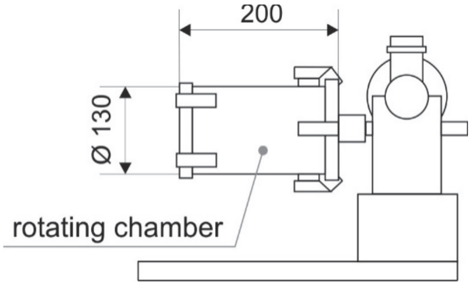

Fig. 2 Schematic set up of the tumbling equipment [4]

Table 1 Testing parameters for mechanical testing and description of characteristic values [4]

Revolutions	900	[---]
Rotation speed	30	[rpm]
Disintegration tendency	$DT = \frac{m_1}{m_0} \cdot 100$	[%]
Abrasion tendency	$AT = \frac{m_2}{m_0} \cdot 100$	[%]

3. EXPERIMENTAL PROCEDURE OF SAMPLE PREPARATION, REDUCTION AND TUMBLING

In order to compare untreated with alkali-soaked material, a representative methodology is essential (descriptive flow sheet in **Fig. 3**). The feeds are globally traded iron carriers, 2 lump ores and 2 pellet brands (refer to **Table 4**). They had been soaked in a 5 molar KOH and NaOH solution for 14 days resulting in alkali adsorption by the lumpy material. Finally the soaked material was dried and sieved (according to ISO 66165 in order to obtain a homogeneous bed feed with particles of 10 - 12.5 mm in size). A subsample was taken for chemical analysis. Two types of tests were operated, a standardized test according to ISO 4695 [6] and an industrial scale process condition test with a temperature and gas composition profile similar to blast furnace (BF) conditions. The industrial scale process conditions test was run at a specific gas ratio of CO and CO_2 with addition of 3 % H_2 (testing parameters for both tests refer to **Table 3**). Both tests were stopped when a reduction degree of 80 % was reached. Tests with non-soaked as well as with soaked materials were performed.

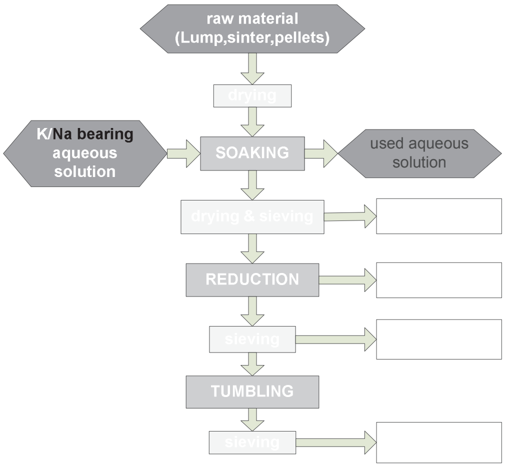

Fig. 3 flow sheet for the evaluation of specific mechanical indices of alkali treated iron carriers

Table 2 Testing parameters of the standardized ISO-test and the industrial scale process conditions reduction test

Test	Phase	Temperature [°C]	Gas composition [vol.-%]	Time [min]
ISO 4695	0	ambient to 950 °C	100 % N_2	60
	I	950 °C	40 % CO, 60 % N_2,	RD_{80}
Industrial scale process conditions	0	ambient to 300 °C	100 % N_2	20
	I	300 - 500 °C	24% CO, 23 % CO_2, 3 % H_2, 50 % N_2	30
	II	500-950 °C	continuous from phase I to phase III	60
	III	950 °C	42 % CO, 5 % CO_2, 3 % H_2, 50 % N_2	RD_{80}

After the reduction tests the material was sieved to determine the grain size distribution before tumbling. The final sieving took place after tumbling and the disintegration and abrasion indices had been calculated with the respective fraction masses received.

4. PETROGRAPHY OF NON-REDUCED MATERIAL

Table 3 Chemical composition of raw materials

Sample	Specific surface area [m²/g]	Fe tot [%]	Fe^{2+} [%]	Al_2O_3 [%]	CaO [%]	K_2O [%]	Na_2O [%]	MgO [%]	SiO_2 [%]	LOI [%]	B_2	B_4
Hematitic ore	0.42	67.0	1.01	0.71	0.02	0.118	0.1	0.01	2.6	0.34	0.0	0.0
Limonitic ore	3.74	63.3	0.76	1.1	0.01	0.004	0.01	0.01	0.01	6.36	1.0	0.0
Pellet brand 1	0.23	64.6	1.38	0.38	0.17	0.08	0.05	0.33	6.34	0.06	0.0	0.1
Pellet brand 2	0.4	65.4	0.26	1.28	2.26	0.02	0.02	0.01	0.5	0.19	4.5	1.3

The analysis data of the raw samples in **Table 4** shows the chemical analysis including the loss on ignition (LOI) and the specific surface area, which was determined by the BET-method. The basicity (B_2/B_4) was calculated in accordance with the chemical analysis. The alkali adsorption of the soaked samples was analysed by chemical analysis and by microprobe mapping. In general the morphological structure of the samples did not change as a result of the treatment. The chemical analyses show an increase in the alkali elements in the soaked samples, yet are different in magnitude due to the different types of the raw materials used. The bar charts in **Fig. 4** show the K_2O and Na_2O contents in the limonitic and hematitic lump ore before and after soaking (grey and black bar respectively). The mapping of the element K with the microprobe proved the increase of alkalis where they were adsorbed more readily by the gangue and limonite than by hematite.

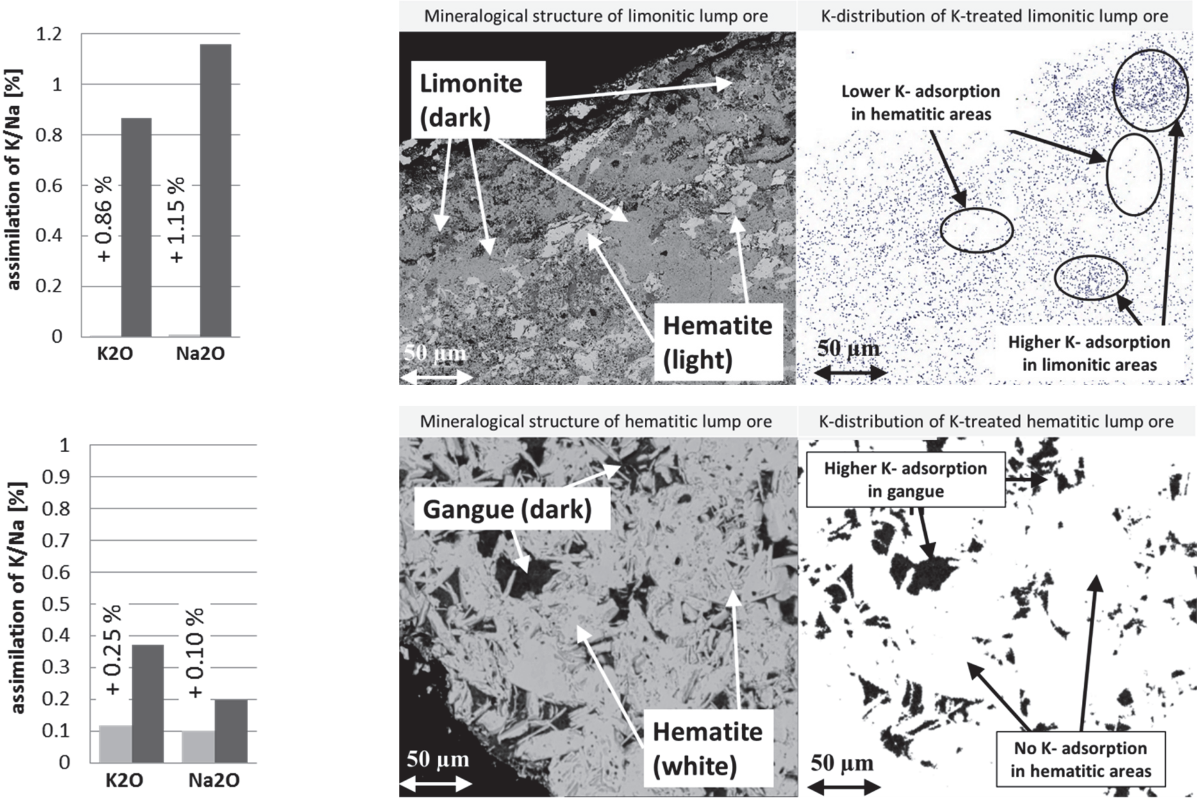

Fig. 4 Chemical analysis and K-mapping of the K-treated lump iron ores (top: limonitic lump ore, bottom: hematitic lump ore)

The pellets show a similar behaviour as the hematitic ore. The alkalis were absorbed mainly by gangue and glassy phases. The increase of K_2O was 1.9 % for pellet brand 1 and 1.1 % for pellet brand 2. The Na_2O content of pellet brand 1 increased from originally 0.05 % to 1.1 % by the soaking (0.02 % to 0.94 % for pellet brand 2). Furthermore, a proportional correlation between molarity of the solution and the assimilation of K and Na was also detectable.

5. MECHANICAL PROPERTIES AFTER REDUCTION AND TUMBLING

The initial grain size of all samples before the reduction tests was 10 to 12 millimetres. **Fig. 5** shows the sieve analysis of the reduced samples after tumbling. The limonitic ore was characterized by a strong affinity to sticking. The surface of the reduced material shows a higher amount of coarse iron whiskers in soaked material compared to the non-soaked ones. Conversely, the portion of fines doubled after tumbling (**Table 5**). Sticking and abrasion effects were always higher in the ISO-tests than under near industrial BF-conditions. Hematitic ore was less affected in relation to limonitic ore- the influence of alkalis on sticking phenomena was similar for both lump brands. Macroscopically both pellet brands were also affected by the addition of alkalis. Due to the grain size distribution Na caused higher degradation of pellet brand 1 whereas K induced higher disintegration rates of pellet brand 2. The different behaviours could be caused by different chemical compositions and different basicity of the gangue. **Fig. 6** shows wustite covered by metallic iron of non-soaked and soaked pellets. In the untreated sample fine porous metallic iron and iron shells were detected. In contrast to that finding the Na-treated sample is characterized by dense iron nuclei on the surface of the wustite grains, by the absence of finely porous metallic iron, by bigger pores and by fewer iron bridges between the grains, thus causing the mechanical properties to deteriorate.

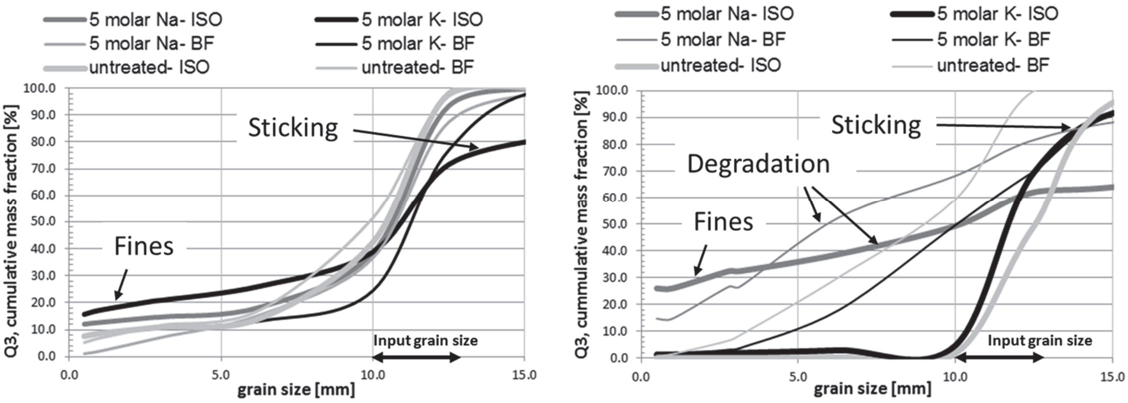

Fig. 5 Grain size distributions of limonitic lump ore (left) and the pellet brand 1 (right); both after tumbling test of treated and untreated material

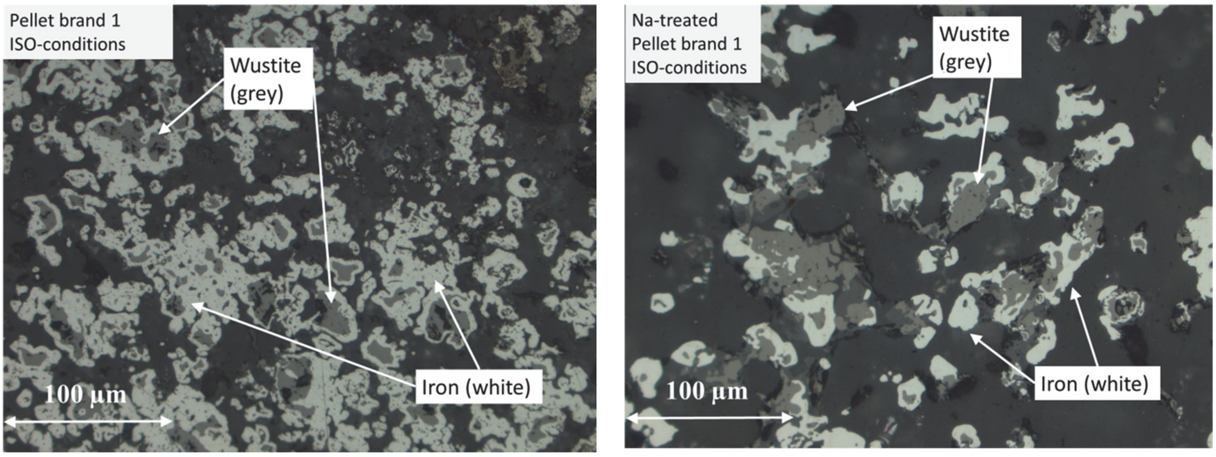

Fig. 6 Micro-photos of untreated and Na-soaked reduced material (ISO 4695 testing conditions)

6. RESULTS

Alkalis show a significant influence on the abrasion, disintegration and formation of iron whiskers, thereby causing enhanced sticking behaviour during the reduction process. Microscopic investigations prove this macroscopic observation. Coarse metallic iron scraps and whiskers on the surface of the wustite grains were primarily found in reduced soaked material. The growth of large iron crystals induces more stress and a higher tendency towards crack formation, respectively. On the basis of the specific mechanical indices of the investigated untreated and treated materials (summarized in **Table 5**) the following conclusions can be drawn:

The change in abrasion tendency of limonitic lump ore is more pronounced under ISO-conditions. The indices under BF-conditions are similar for both treated and untreated material. Abrasion of hematitic lumps was hardly affected by alkali addition. The biggest influence on disintegration and abrasion was detected on limonitic ore reduced under ISO-conditions. All lump ores showed increased sticking tendency.

Pellets comprise more complex correlations on the addition of alkalis. Not all treated materials indicated significant changes in the mechanical indices. However, Na-treated pellet brand 1 showed a very high degradation tendency during reduction under ISO- conditions. Under near BF- conditions both pellet types showed poorer mechanical stability. Although some degradation of the particles was also detected on untreated material, the amount of fines increased significantly.

Table 4 Comparison of specific mechanical indices according to different reduction conditions and different amounts of alkalis in the material

Sample	Reduction test at ISO- conditions						Reduction test at industrial scale conditions (BF)					
[values in %]	non soaked material		K-soaked material		Na-soaked material		non soaked material		K-soaked material		Na-soaked material	
	DT	*AT*	*DT*	*AT*	*DT*	*AT*	*DT*	*AT*	*DT*	*AT*	*DT*	*AT*
Hematitic ore	89.5	2.4	85.1	4.2	89.9	2.2	88.0	0.9	88.0	1.8	88.3	1.0
Limonitic ore	86.8	7.4	73.8	15.7	81.6	12.1	82.6	5.2	86.8	7.9	84.5	1.1
Pellet brand 1	99.3	0.3	95.3	1.4	50.8	26	69.5	1.3	52.9	4	47.6	14.7
Pellet brand 2	96.5	1.6	95.9	0.9	85.8	6.5	96.2	0.85	47.7	16.7	89.5	1.2

CONCLUSION

Lumpy iron carriers as lump ore and pellets are significantly affected by alkalis. An increase of sticking behaviour, of the amount of fines and the general degradation was determined by reduction and tumbling tests. Under the microscope coarser metallic iron nuclei were observed in soaked materials as opposed to in untreated ones. This confirms the action of alkalis on the iron formation mechanism during reduction and, as a consequence, the following degradation of the product. As a matter of course, testing parameters control the variables; at ISO- and BF- reduction conditions the abrasion and disintegration behaviours of the iron carriers were significantly different. The variation of the mechanical indices between the two pellets brands is higher, which indicates the influence of the basicity on the effect of alkalis on disintegration.

ACKNOWLEDGEMENT

This work has been performed within the K1-MET, member of COMET - Competence Centers for Excellence Technologies, and is financially supported by voestalpine Stahl GmbH, voestalpine Stahl Donawitz GmbH, Siemens VAI Metals Technologies GmbH, the BMVIT, BMWFJ, the provinces of Upper Austria, Styria and Tyrol, SFG and Tiroler Zukunftsstiftung. COMET is managed by FFG (Austrian research promotion agency).

REFERENCES

[1] ABRAHAM, K.P., STAFFANSSON, L.I., The Alkali Problem in the Blast Furnace, *Scandinavian Journal of Metallurgy*, 4, 1975, pp 193-204.

[2] ENDE, H., GREBE, K., THOMALLA, S., Alkalien als Ursache von Schwell- und Zerfallsvorgängen bei der Reduktion von Eisenerz, *Stahl und Eisen*, 90, 1970, pp 667-676.

[3] GUPTA, S., FRENCH, D., SAKUROVS, R., GRIGORE, M., SUN, H., CHAM, T., Minerals and iron-making reactions in blast furnaces, *Progress in Energy and Combustion Science*, 34, 2008, pp. 155-197.

[4] HANEL, M. B., MALI, H., SCHENK, J.L., SKORIANZ, M., HAUZENBERGER, F., THALER, C.; STOCKER, H., Characterization of Different Lump Ore Brands According to Industrial Scale Process Conditions by Means of Reducibility Testing and Morphological Investigation, *Proceedings of AISTech2013- Pittsburgh*, USA, 2013, 447-456.

[5] HANEL, M.B., MALI, H., SCHENK, J.L., SKORIANZ, M., HAUZENBERGER, F., THALER, C.; STOCKER, H., Characterization of burden material for ironmaking by means of reduction tests with morphological characterization, *Proceedings of the 14th ISIJ-VDEh-Jernkontoret Joint Symposium- Osaka*, Japan, 2013, 145-153.

[6] International Organization for Standardization: ISO 4695 Iron ores - Determination of reducibility (1995)