

CO Reactivity of Manganese Lumps Versus Briquettes

Leandro Gustavo Mendes DE JESUS^{1)*} and Merete TANGSTAD²⁾

1) Federal Institute of Education Science and Technology of Mato Grosso do Sul, Department of Metallurgy, Corumbá, 79310-110 Brazil.

2) Norwegian University of Science and Technology/Department of Materials Science and Engineering, Trondheim, 7034 Norway.

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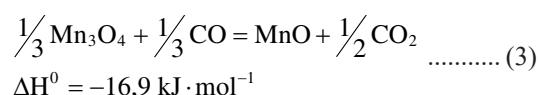
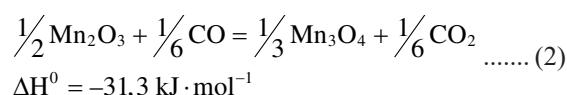
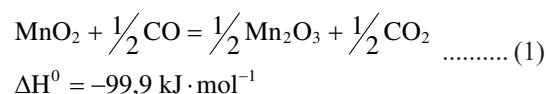
In this work, a comparison between CO reactivity of lumps and briquettes made of two different binder and three different raw materials is presented. Experimental results on the prereaction behavior of such materials in 70% CO and 30% CO₂ atmosphere, heating rate of 0,17 K/s (10°C/min) at temperatures up to 1 100°C are discussed. It was shown that briquettes presented higher CO reactivity, especially those whose molasses was the binder which had the highest reactivity. Level of oxygen also played an important role in CO reactivity. Comilog and Urucum with the highest oxygen level had highest reactivity while Assmang with the lowest oxygen level had the lowest reactivity between the raw materials. Porosity was a key variable to explain CO reactivity. Molasses briquettes had the highest porosity and the highest CO reactivity followed by bentonite briquettes and lumps.

KEY WORDS: manganese ore fines; pre-reduction; briquettes; CO reactivity.

1. Introduction

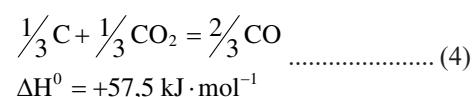
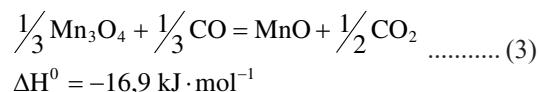
During mining and mineral processing of manganese ore between 30 and 60% of the material extracted from the mine is treated as waste.¹⁾ Even though such materials have similar chemical composition as the manganese ferroalloy producers require, they are much finer than what is acceptable in submerged arc furnaces. Despite being challenging, to improve the usage of fines in the furnace could be interesting, both economically and environmentally. It would lower the amount of tailings and increase the usage of the reservoir. Agglomeration processes were designed as a solution to enhance the usage of fines in metallurgical processes. Briquetting stands as a low investment and operational costs and would be one of the interesting agglomeration techniques reducing the waste material.

When the manganese materials are charged into the furnace, it is desired that higher manganese oxides are reduced in the solid state to MnO at temperatures lower than 800°C, as it is believed that the undesirable Boudouard reaction starts around this temperature. During the reduction processes the unstable higher manganese oxides MnO₂, Mn₂O₃, Mn₃O₄ will be reduced with CO gas. Hence, the manganese oxide, MnO_x will be reduced to MnO, where the x ranges from 2 down to 1. The reduction reactions are reduced by the following reactions:¹⁾



Ideally, the heat produced by the electric current flowing through the coked zone promotes reduction of MnO to manganese metal releasing CO at high temperatures (1 400–1 600°C). The ascending CO gas heats the charge promoting the mentioned reactions.

However, if the pre-reduction is not finished before the charge temperature reaches 800°C, the reaction path will be different as shown in the following:



* Corresponding author: E-mail: leandro.mendes@ifms.edu.br



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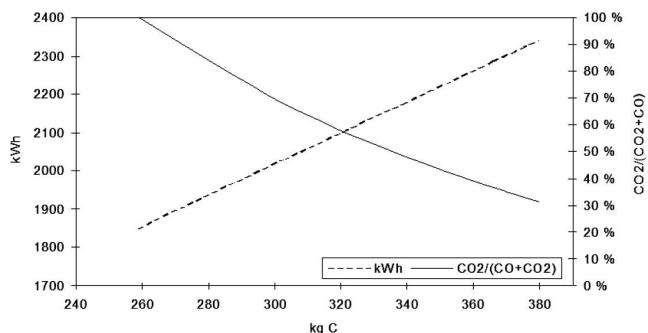
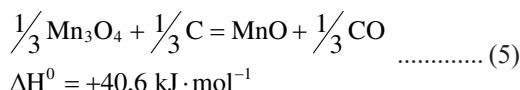


Fig. 1. The relation between coke consumption, the $\text{CO}_2/(\text{CO} + \text{CO}_2)$ ratio and the consumption of electric energy for production of HCFeMn from a random charge.²⁾



The pre-reduction will be carried out through the Bouard reaction which is highly endothermic. Thus, there will be an increase of the coke consumption and a higher demand of electrical energy.

The degree of pre-reduction defined by Tangstad²⁾ is expressed by the off-gas ratio ($\text{CO}_2/(\text{CO}_2 + \text{CO})$) and is directly related to the coke and energy consumption as showed in **Fig. 1** for a fixed charge. The lowest the ratio the highest the degree of pre-reduction.

In this paper, the degree of pre-reduction, which is also the CO reactivity, of briquettes made of three different manganese raw materials and two different binders will be measured and compared with lumps of the same materials. As stated by Turkova *et al.*³⁾ the CO reactivity was defined as the ability of manganese materials to be reduced to MnO by CO gas in a temperature range from 0°C to 800°C. The porosity of the materials will also be measured to see its effect on the CO reactivity.

2. Apparatus and Procedures

2.1. Materials

The manganese materials used in this paper were Comilog ore from Gabon and Assmang ore from South Africa in form of lumps. Urucum tailing dam's material was collected in the city of Corumbá in Brazil and was provided as fines.

The lumpy material was 9–15 mm particles. In order to produce briquettes, the lumpy ores (Comilog and Assmang) materials were first crushed and sieved. The Urucum material was also sieved. All materials used in the briquettes was – 250 µm. The size distribution of the raw materials is shown in **Table 1**.

The materials were chemical analyzed by X-ray fluorescence while the MnO_2 amount was obtained by titration. **Table 2** shows the chemical analysis of the raw materials.

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As binders, two different materials were used, molasses and bentonite. Molasses is a byproduct of the sugar cane refining and has a very wide composition. The main components are carbohydrates and water.⁴⁾ Bentonite is

Table 1. Briquette's raw material size distribution.

Raw material	Retained [%]				
	250 µm	100 µm	63 µm	45 µm	0 µm
Comilog	0,00	48,35	71,65	82,59	100,00
Assmang	0,00	37,79	50,78	58,33	100,00
Urucum	0,00	67,96	81,71	88,28	100,00

Table 2. Raw materials chemical composition, mass% (L=lumpy ore, B=briquettes, analyzed by SINTEF Molab).

Compound	Comilog		Assmang		Urucum	
	L	Bq	L	Bq	L	Bq
Mn_{tot}	48,08	46,15	46,87	45,05	42,22	27,28
MnO_2	71,35	66,16	34,91	33,70	62,13	40,43
Fe_{tot}	6,62	3,56	7,52	9,63	15,69	28,16
SiO_2	2,93	6,53	4,11	5,65	1,70	9,11
Al_2O_3	5,05	8,12	0,46	0,45	1,28	2,93
CaO	0,08	0,40	8,25	7,60	0,17	0,20
MgO	0,10	0,11	1,82	1,15	0,14	0,10
TiO_2	0,13	0,21	0,01	0,02	0,09	0,21
P	0,18	0,17	0,05	0,03	0,15	0,25
S	0,02	0,01	0,06	0,33	0,05	0,04
K_2O	0,90	1,00	0,04	0,01	3,32	1,73
BaO	0,18	0,23	0,17	0,93	0,21	0,29
H_2O	0,39	0,62	0,00	0,04	0,00	0,00

a clay mineral which consists mostly of montmorillonite with chemical formula of $(\text{Na},\text{Ca})_{0,33}(\text{Al},\text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot \text{nH}_2\text{O}$.⁵⁾ The molasses briquettes were made with the mass percentage of 10% of binder while the bentonite briquettes had a mass percentage of 5%. Results obtained by By⁶⁾ were used to set the binder content.

2.2. Production of the Briquettes

The raw materials were mixed for 2 minutes and the mixture was pressed by the use of an axial press, a stainless-steel die and a punch of 10 mm of inner diameter with a pressure of 100 MPa. After the pressure in the axial press was reached, it was kept for 30 seconds before the briquette was released.

2.3. Apparatus and Test Description

The CO reactivity test was performed in a thermogravimetric furnace. **Figure 2** shows a picture of the furnace and a diagram of the crucible. The crucible was charged with around 100 g of materials as briquettes or lumpy ore.

The CO reactivity test consisted of heating the sample with a heating rate of about 0,17 K/s (10°C/min) for 110 minutes, finishing the test at 1 100°C. The furnace heating and heating rate is controlled by a thermocouple located on the furnace wall. There is also a thermocouple recording the temperature within the crucible, since the reactions can absorb or release heat causing deviations between the furnace temperature and the crucible temperature.

During the heating of the sample a gas mixture consisting of 70% CO and 30% CO_2 was charged inside the crucible, the gas mixture flowrate was $6,67 \cdot 10^{-5} \text{ m}^3/\text{s}$ (4 Nlpm). The gas is heated in the double walled crucible and will hence

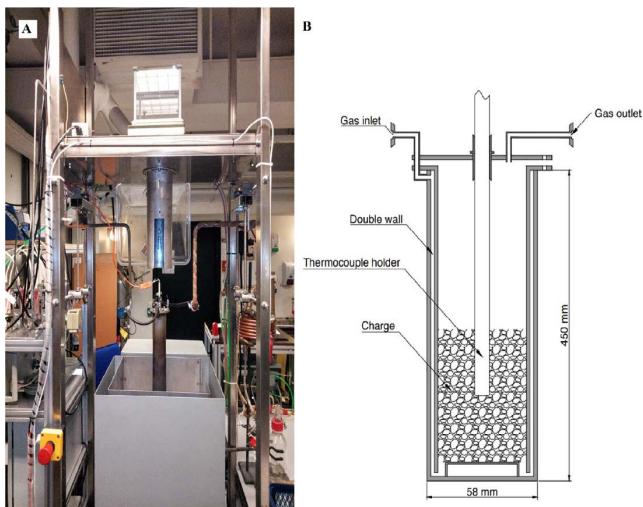


Fig. 2. Retort thermogravimetric furnace (A) and a diagram of its crucible (not to scale, B). (Online version in color.)

have a high temperature when seeing the material. When the test was finished, the furnace power was turned off and argon was flushed at a flowrate of $1,67 \cdot 10^{-5} \text{ m}^3/\text{s}$ (1 Nlpm) for 45 minutes to quench the sample and avoid re-oxidation of the sample.

2.4. Porosity Tests

Before and after the CO reactivity tests were performed, three briquettes/lumps were sampled, and their porosity was assessed. The porosity was measured by the ratio between the envelope volume and the pore volume. The envelope volume test was performed by a GeoPyc 1360 pycnometer. The pore volume was taken by an AccuPyc 1330 helium pycnometer.

3. Results and Discussion

The measured parameters obtained during experiment is showed by **Fig. 3**. Crucible temperature, furnace temperature, mass loss, CO and CO₂ content in the off-gas are plotted. In addition, the mass before and after the experiment is measured. In order to obtain the MnO_x versus temperature some assumptions were made. For instance, in the comparison between lumpy ore with molasses briquettes, it is not possible to convert the mass, and its loss, into MnO_x directly, since molasses is evaporated and shift the final mass loss as well as the mass loss behavior. Therefore, to neutralize such effects the CO₂ function in the off-gas, g(t), was used to determine the x from the MnO_x behavior as function of temperature. Assuming that all manganese ore reduction will result into a higher CO₂ concentration in the off-gas it is possible to relate these data with the reaction course.

Thus, the instant x values, x_i, from the MnO_x were calculated by the CO₂ in the gas analysis. The x value is ranging from the initial x value, x₀, to the final x value, x_f which are obtained by the chemical analysis. The behavior of the curve was given by the rate between the amount of gas generated up to the moment, g(t_i), and the total amount of gas released, g(t_f). The mathematical expression is given by:

$$x_i = \left(1 - \frac{g(t_i)}{g(t_f)}\right) \cdot (x_0 - x_f) + x_f \dots \dots \dots (6)$$

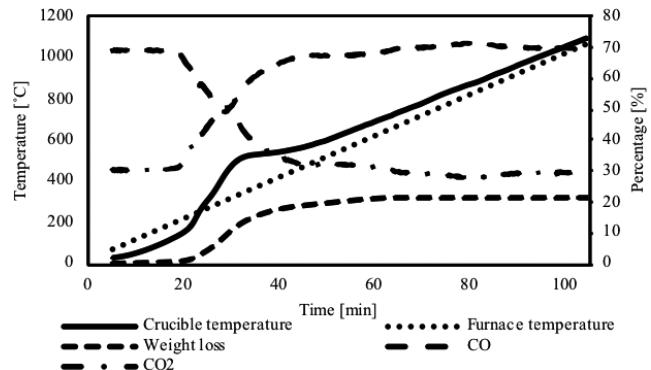


Fig. 3. Typical raw data obtained by a test in the furnace with Comilog and molasses briquettes.

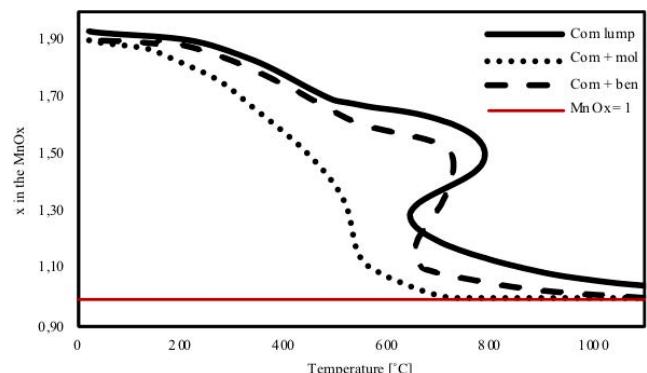


Fig. 4. The calculated MnO_x of Comilog materials. (Online version in color.)

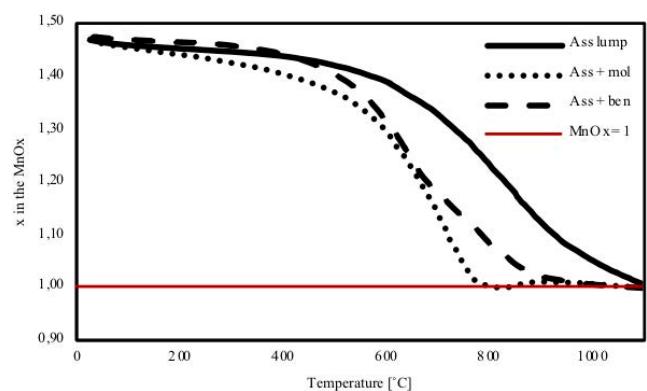


Fig. 5. The calculated MnO_x of Assmang materials. (Online version in color.)

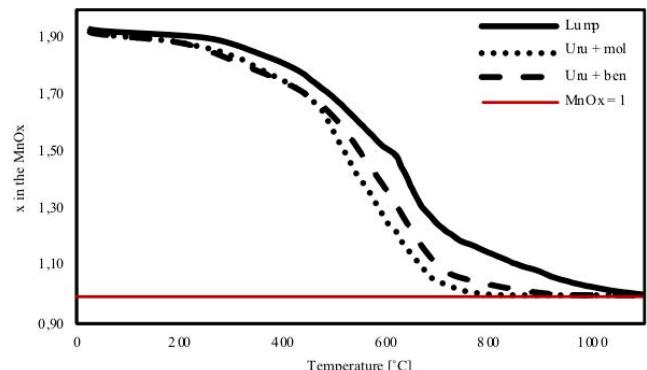


Fig. 6. The calculated MnO_x of Urucum materials. (Online version in color.)

Figures 4 to 6 show the x in the MnO_x versus crucible temperature. It can be seen that when the temperature increases the reduction proceeds. The further increase on the temperature within the crucible due to the exothermic reactions can also be noticed. This effect is noticed in higher extent in Comilog samples due to higher oxygen levels (Fig. 4). It was not possible to distinguish the different oxides reduction as there is a continuous mass loss, which was previously observed by other authors.⁷⁻⁹⁾ In addition, the reduction behavior of briquettes in comparison with lumps reveal that agglomerates behaved as fines where the reaction started at lower temperatures as previously observed by Welham.¹⁰⁾

It can also be seen that for briquettes with molasses, at 800°C the reduction is finished. This is not the case for bentonite briquettes nor lumpy material. Comilog lumps was not reduced completely to MnO even after it reached 1 100°C.

Table 3 shows the calculated MnO_x , at 800°C. The chemical composition of the materials after the experiments is shown in **Table 4**. It can be noticed from Figs. 4–6 that briquettes and lumps of all the raw materials with the exception of Comilog have been reduced to MnO at the end of the experiment. Despite the reduction path of the different raw materials are different, the CO reactivity of molasses briquettes is similar, since all the materials were completely reduced to MnO at 800°C. The bentonite briquettes also behave similarly, as they reached similar x values at 800°C between 1.02 to 1.05.

Comilog and Urucum lumpy ore at 800°C has relatively similar CO reactivity. The amount of oxygen left in the ore is 1,14 in Comilog and 1,15 in Urucum. The high x values in its initial composition, 1,94 and 1,92 respectively, indicates that these two raw materials are mainly composed by MnO_2 and at 800°C the reduction is somewhere between the Mn_3O_4 ($x = 1,33$) and MnO ($x = 1,00$) at 800°C. However, when the test was finished only Urucum raw material was completely reduced while Comilog was mostly reduced. Assmang lumpy material started with $x = 1,47$ corresponding to a Mn_2O_3 composition. At 800°C it's the oxygen level was somewhere between Mn_3O_4 and MnO.

The MnO_x versus temperature for Comilog lumpy ore has a high increase of temperature, followed for a smaller temperature increase in lumpy Urucum. This is explained

Table 3. Calculated MnO_x of materials at 800°C.

Compound	Comilog			Assmang			Urucum		
	L	M	B	L	M	B	L	M	B
MnO_x	1,14	1	1,05	1,23	1	1,05	1,15	1	1,02

Table 4. Chemical composition of materials after CO reactivity tests at 1 100°C, mass%.

Compound	Comilog			Assmang			Urucum		
	L	M	B	L	M	B	L	M	B
Mn_{tot}	67,25	50,79	53,72	57,14	51,54	53,37	56,54	31,71	30,29
MnO_2	4,77	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
Fe_{tot}	1,83	10,96	4,36	8,70	11,01	8,64	9,95	32,39	30,60

by the high amount of MnO_2 in the ore and consequent high release of heat due to the exothermic prerduction reactions, reaction (1). Comilog and Urucum briquettes did not present the same effect due to its particle size. Even though the briquettes were agglomerated to bigger sizes it seems that during reduction they behaved as fines which resulted in lower increase in temperature as observed by Pochart *et al.*¹¹⁾ This is due to the fact that the reduction of MnO_2 starts sooner and will hence be reduced over longer time. As Assmang ore has lower initial oxygen content, that is Mn_2O_3 , the same heating was not present. Such trend between Comilog and Assmang ore reactivities was already observed by Berg and Olsen.¹²⁾

The raw materials with the higher oxygen content presented a higher reactivity and the same trend was observed by other authors.^{3,7,8,10,13-15)} Thus, Urucum ore and Comilog ore have higher reactivity than Assmang ore. In general, the CO reactivity can also be ranked by the form of the material that is being reduced from the highest to the lowest, as following: molasses briquettes, bentonite briquettes and lumpy ore.

As it was previous mentioned, the excess of oxygen that remains after 800°C will not be reduced by CO gas. This means that it is considered that any oxygen excess, other than $x = 1$, will reduce through the carbon gasification, Reaction 5. Such assumption means a higher carbon consumption for materials that were not completely prerduced to MnO at 800°C. **Table 5** shows the additional carbon consumption that every material would require.

Despite Comilog and Urucum lumps starts with a higher oxygen content their high reactivity leads to lower carbon consumption. Assmang lumps is hence the material with the lowest reactivity and will hence consume more carbon. The briquettes made with molasses as binder are completely prerduced at 800°C, hence, they do not demand any additional carbon material. These ores also release high amount of energy during the pre-reduction due to exothermic reactions. The bentonite briquettes have similar behavior as the molasses briquettes but with lower reactivity demanding lower additional carbon than lumps. It can clearly be noticed that briquettes have higher reactivity and the binder will determine the CO reactivity more than the difference between the ores.

Table 5. Additional carbon consumption per ton of manganese in the raw material for reduction above of higher manganese oxides in Boudouard reaction active zone.

Material	Type	MnO_x value at 800°C	Carbon, kg/ton of Mn
Comilog	L	1,14	249,4
	M	1,00	218
	B	1,05	229,3
Assmang	L	1,23	268,6
	M	1,00	218
Urucum	B	1,05	229,3
	L	1,15	251,2
	M	1,00	218
	B	1,02	222,8

It is possible to conclude, from the point of view of the manganese ferroalloys industrial process, that briquettes made with molasses as binder will provide the most beneficial effect on carbon and energy consumption. Such favorable effect occurs mainly in the Comilog and Urucum briquettes, since they will not demand additional carbon consumption and also that their high amount of oxygen result in high energy release. The use of bentonite as binder reduces the performance of the briquettes raising the carbon consumption. Furthermore, the use of lumpy material would cause a negative effect, since they have shown relatively low CO reactivity, thus, the highest carbon consumption. Among the lumpy materials, Assmang performed with the lowest CO reactivity, consequently, has the highest theoretical carbon consumption. The lowering in coke consumption and energetical advantages of the usage of agglomerates was already pointed in other studies.^{3,13,14,16)}

The porosity tests of the sampled briquettes specimens and lump particles are shown in **Table 6**. In order to compare the porosity of the different raw materials, the mean values between three measurements were used. The porosity of molasses briquettes was considered to be the tested sample porosity, since their green porosity was very low due to the molasses which spread through the pores and voids between the agglomerate particles. However, as studied by Flores *et al.*¹⁷⁾ molasses is decomposed at around 200°C. Hence, it is assumed that additional porosity, mentioned by Turkova,³⁾ created by removal of bound water, CO₂ from carbonates and reduction of manganese oxides was negligible when compared with the porosity left by the molasses

decomposition.

The higher temperature increase noticed between 600°C and 800°C presented in the case of Comilog lumps and Comilog bentonite briquettes (Fig. 4) may also be explained by the lower porosity presented in such materials. The same characteristics were observed by Pochart *et al.*¹¹⁾ which showed that materials whose interstitial space is lower presented higher increase due to the exothermic reactions.

The results of CO reactivity experiments are also plotted versus porosity in **Fig. 7**. It can be seen that a high porosity leads to high CO reactivity which leads to a lower oxygen content at 800°C which is accordance with other studies.^{3,13,14,18)} This is believed to be due to diffusion of CO in and CO₂ out through the product layer being rate determining, which was observed by Berg and Olsen.¹²⁾

4. Conclusions

The work presented a comparative study on CO reactivity and porosity between lumps and briquettes with two different binder of three different raw materials. It was found that Comilog and Urucum materials have higher CO reactivity than Assmang. Through the work it was found that high porosity affects positively the CO reactivity which corroborates with previous works performed on the subject. As consequence, briquettes performed better than lumps of the same ore. The molasses decomposition enhances the porosity of molasses briquettes leaving them as the ones with higher reactivity when compared with lumps and bentonite briquettes.

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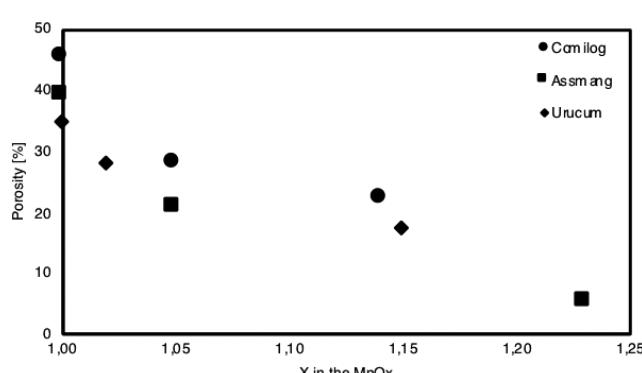


Fig. 7. Porosity versus the calculated x in MnO_x at 800°C.