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# Steel waste used in reducing emissions of nitrous oxide

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**ABSTRACT.** Gross wastes of the steel industry were evaluated as catalyst for the reduction of nitrous oxide. The wastes were obtained from steel mill residues (MS), lamination (LA), quenching (QC) and blast furnace powder (BF) and characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD) and hydrogen temperature-programmed reduction ($H_2$-TPR). Results revealed Si, Ca, S, Rh, Fe, Cr, Mn and Cu for all wastes, with iron featuring the greatest amount. $H_2$-TPR analyses showed $H_2$ consumption peaks associated with rhodium oxide, also detected by XRF. The content of comparative rhodium oxide in samples was: MS > LA > QC > BF. $N_2O$ conversion increases with increase in temperature for all catalysts. The activity of the catalysts MS > LA > QC > BF was related to rhodium oxide rate in the wastes.

**Keywords:** greenhouse gas, reuse, characterization, catalyst, pollution.

## Resíduos siderúgicos usados na redução das emissões de óxido nitroso

**RESUMO.** Neste trabalho, os resíduos brutos da indústria siderúrgica foram avaliados como catalisador para a redução de óxido nitroso. Os resíduos foram obtidos de aciaria (MS), laminação (LA), têmpera (QC) e pó de alto-forno (BF). Os resíduos foram caracterizados por fluorescência de raios X (FRX), difratometria de raios X (DRX) e redução com hidrogênio a temperatura programada (RTP-$H_2$). Os resultados mostraram a presença de Si, Ca, S, Rh, Fe, Cr, Mn e Cu para todos os resíduos, mas o ferro foi o elemento em maior quantidade. A análise de RTP-$H_2$ mostrou picos de consumo de $H_2$ que foram associados com a presença de óxido de ródio, como também observado por XRF. O conteúdo de óxido de ródio comparativo nas amostras foi: MS > LA > QC > BF. Observou-se que a conversão de $N_2O$ aumenta com o aumento da temperatura para todos os catalisadores. A atividade dos catalisadores MS > LA > QC > BF foi relacionada com o teor de óxido de ródio nesses resíduos.

**Palavras-chave:** gás de efeito estufa, reuso, caracterização, catalisador, poluição.

## Introduction

One of the challenges facing mankind in the 21st century is the use of waste and its management. Since world production of waste reaches millions of tons per day, solutions to minimize economic costs and environmental impacts from industrial waste are necessary and urgent (Stead & Stead, 2015). The steel industry produces worldwide 1.338 million tons of crude steel per year and, in addition, 50 million tons of waste. In Brazil, the annual steel production is 34 million tons and approximately 1.6 million tons of recyclable waste are produced yearly. Steel is manufactured from iron ore mostly by blast furnace (BF), basic oxygen furnace (BOF) and electric arc furnace (EAF), the latter when manufactured from scrap materials. The steel industry, a major consumer of energy and materials, also accounts for considerable volumes of gas emissions, liquid effluents and solid waste, due to the large amounts of physical-chemical reactions involved in the various stages of the steel-manufacturing process (Carvalho, Mesquita, & Araújo, 2015). Coke oven by product plant, sintering, reduction in the blast furnace and steel melting shop are the steps with higher amounts of iron-rich solid waste and gases emissions. Dumping solid waste on open space and in excavated earth pollutes the environment with dust and leachate and produces huge financial liability.

The reduction of gas emissions implies in minimizing environmental losses associated with climate change, acidification of ecosystems and formation of photochemical smog (Colpini et al., 2013). In the steel industry, NOx are the most dangerous in gas emissions due to their contribution in greenhouse gas and significant ozone-depleting emissions to the atmosphere. Among nitrogen oxides, nitrous oxide ($N_2O$) is the most abundant in the atmosphere and a major contributor to the greenhouse effect and the depletion of the ozone layer (Oenema et al., 2014). According to the guidelines of the Intergovernmental Panel on Climate Change (IPCC), the global warming potential (GWP) for a 100-year-time horizon is about 298 times for $N_2O$ when compared with that of $CO_2$, on a weight basis (Pardo, Moral, Aguilera, & Prado, 2015).

The solid wastes from any industry may be used as catalysts in the treatment of gaseous effluents (Oliveira, Fabris, & Pereira, 2013). Consequently, it is worthwhile to use low cost catalysts to reduce the overall cost of the treatment process and, at the same time, keep reasonable efficiency. In current study, the wastes produced by the steel industry were used as catalysts in the $N_2O$ decomposition reaction. As a rule, the steel industry produces large amounts of solid wastes while processing materials through its various procedures. Solid waste from the conventional process, including furnace slag and collected dust, is generated at an average rate ranging between 300 kg $t^{-1}$ of steel and 500 kg $t^{-1}$ (Ali, Gad-Allah, & Badawy, 2013). These solid wastes have many valuable products which may be reused if recovered economically. Wastes are actually rich in iron and may be used as catalyst in reducing emissions of nitrous oxide. The use of iron-containing waste in the treatment of nitrous oxide will surely reduce the cost of gases treatment. Current analysis focuses on the use of iron-containing waste as a heterogeneous catalyst in the reduction of industrial emissions of nitrous oxide.

## Material and methods

### Characterization of steel industry wastes

The wastes used in current research are from the steel industry, obtained from melt shop, lamination, quenching and powder blast furnace. They were characterized and used as catalyst in nitrous oxide reaction without any pretreatment. The catalysts were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD) and hydrogen temperature-programmed reduction ($H_2$-TPR). Characterization by fluorescence allows qualitative and quantitative analysis of the elements of a given sample. XRF analyses were carried out in equipment Shimadzu EDX 720/800HS with 200 mg of catalyst and a flow of 200 mL $min.^{-1}$ of He. XRD analyzes were performed by the powder method on a Rigaku diffractometer (Miniflex 600) with Cu tube, Ni-filtered, operating at 40 KV, 15 mA and CuKα radiation (λ = 0.1542). The speed of the goniometer used was 2° (2θ) $min.^{-1}$, the angle ranging between 10 and 80° (2θ). The identification of crystalline phases present in melt shop, lamination, quenching and powder blast furnace wastes was based on the comparison with Diffraction Standards from Database X'Pert HighScore (2001).

$H_2$-TPR analyses were performed on SAMP3 equipment (Termolab Equipment, Brazil) with a flow of 30 ml $min.^{-1}$ from a mixture of 2% $H_2$/Air, heating rate 10°C $min.^{-1}$ in which hydrogen consumption was monitored by a thermal conductivity detector.

### Catalytic evaluation of steel industry wastes

Wastes were used as catalysts in the reaction of nitrous oxide decomposition. A tubular fixed bed reactor containing 50 mg of catalyst was employed in the catalysis tests. The reactor was fed with a 50 ml $min.^{-1}$ continuous gas flow containing 10% $N_2O$ in He, and the reaction was carried out between 100 and 600°C, heated to 10°C $min.^{-1}$. Reactant and products were continuously analyzed with a gas analyzer system at each temperature (Pfeiffer, Thermo star GSD 320 T model) reviewing the following masses: He (4), $N_2$ (28), $O_2$ (32), NO (30) and $N_2O$ (44). Errors in catalytic activity measurements lay between 3 and 5%.

The catalytic activity of the steel industry wastes in the $N_2O$ decomposition reaction was measured in terms of $N_2O$ conversion to $N_2$ and $O_2$, calculated by Equation 1.

$$Conversion\ (\%) = \frac{100 * [(N_2O)_{in} - (N_2O)_{out}]}{(N_2O)_{in}} \qquad (1)$$

## Results and discussion

Tables 1 and 2 show X-ray fluorescence (XRF) results of the samples from melt shop (MS), lamination (LA), quenching (QC) powder and blast furnace (LF). Qualitative results in Table 1 show that the chemical elements Si, Ca, S, Rh, Fe, Cr, Mn and Cu occur in all samples. The additional presence of P and Mo may be observed in the lamination sample, while P, Zn, Sr and Zr are identified in the melt shop sample. Pb and K are reported in the blast furnace powder sample.

**Table 1.** Results of qualitative analysis by X-ray fluorescence.

| Catalyst | Composition |
|---|---|
| Melt shop (MS) | Si, Ca, P, S, Rh, Fe, Cr, Mn, Cu, Zn, Sr, Zr |
| Lamination (LA) | Si, Ca, P, S, Rh, Fe, Cr, Mn, Cu, Mo |
| Quenching (QC) | Si, Ca, S, Rh, Fe, Cr, Mn, Cu |
| Powder blast furnace (BF) | Si, Ca, S, Rh, K, Fe, Cr, Mn, Cu, Zn, Sr, Pb |

Table 2 shows the XRF quantitative results from waste of melt shop (MS), lamination (LA), quenching (QC) and powder blast furnace (BF). Note that Pb and Rh appear only in qualitative results, probably due to their low content in the samples. The major presence of iron oxide may be observed for all wastes (Table 2). However, the amounts of iron oxide from melt shop (68.96%) and powder blast furnace (61.56%) were lower when compared to lamination (91.10%) and quenching (93.80%) wastes, due to the production process, i.e., the melt shop waste has been mixed with slag. This fact is evidenced by high amounts of calcium oxide and silicon oxide in the composition of melt shop waste (Mourão et al., 2007). Calcium silicate, a mineral called Wollastonite, may be formed in the blast furnace (Amin & Oza 2015; Santos et al., 2014). The volatility of zinc and its condensation in a cooler region of the furnace produces high zinc oxide content in the powder blast furnace waste.

**Table 2**. Results of quantitative analysis by X-ray fluorescence

| Component | Melt shop (% w w$^{-1}$) | Lamination (% w w$^{-1}$) | Quenching (% w w$^{-1}$) | Powder blast furnace (% w w$^{-1}$) |
|---|---|---|---|---|
| $Fe_2O_3$ | 68.96 | 91.09 | 93.80 | 61.56 |
| ZnO | 0.10 | - | - | 14.91 |
| CaO | 9.35 | 0.18 | 0.11 | 12.14 |
| MnO | 1.86 | 0.89 | 0.98 | 4.43 |
| $SiO_2$ | 16.53 | 3.50 | 2.83 | 3.31 |
| $SO_3$ | 1.95 | 1.95 | 1.46 | 2.09 |
| $K_2O$ | - | - | - | 0.97 |
| $Cr_2O_3$ | 0.43 | 0.44 | 0.77 | 0.50 |
| CuO | 0.04 | 0.07 | 0.05 | 0.05 |
| SrO | 0.04 | - | - | 0.04 |
| $P_2O_5$ | 0.57 | 1.84 | - | - |
| $ZrO_2$ | 0.17 | - | - | - |
| $MoO_3$ | - | 0.03 | - | - |

Other metals such as manganese, chromium, copper, rhodium and others, from scrap, may also occur in the wastes, albeit in less amounts. It should be enhanced that Fe, Cu and Rh are metals that have catalytic activity in the $N_2O$ decomposition reaction (Taniou, Ziaka, & Vasileiadis, 2013). It has not been possible to quantify the Rh content on the wastes due to its low content, probably due to the fact that it lies below the equipment´s detection limit (0.01%).

Figure 1 shows the results of X-ray diffraction (XRD) of waste from melt shop, lamination, powder blast furnace and quenching. XRD patterns make possible the identification of the characteristic peaks that confirm the presence of hematite (Xpert N. 02-0915), magnetite (Xpert N. 04-0755), copper oxide (Xpert N. 03-0867), chromium oxide (Xpert N. 04-0765) calcium silicate (Xpert N. 02-0689) and manganese oxide (Xpert N. 04-0326). Silicon dioxide (Xpert N. 01-0649) has been reported in blast furnace powder and lamination wastes. Zinc oxide (Xpert N. 03-0888) and franklinite ($ZnFe_2O_4$) were respectively identified in the melt shop and powder blast furnace wastes (Martins, Neto, & Cunha, 2008). Peaks attributed to zirconium dioxide (Xpert N. 05-0543) were observed only in the melt shop sample. XRD results corroborate those reported in XRF.

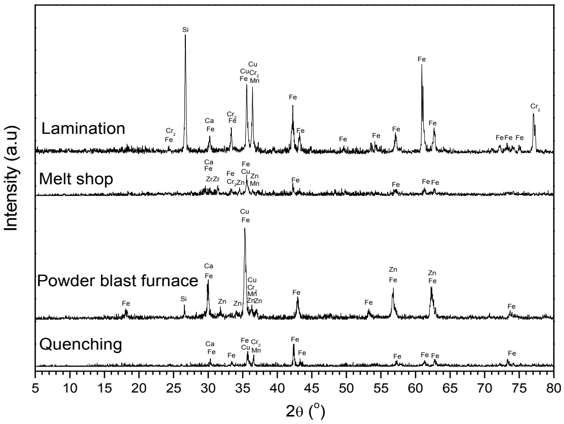

**Figure 1.** Results of X-ray diffraction of catalysts

The presence of iron (hematite and magnetite) is expected since the waste from the melt shop and powder blast furnace involved pig iron to be transformed into various types of steel. The process of quenching is the abrupt heating and cooling of metal to increase hardness and may generate hematite waste during processing. A characteristic peak at $2\Theta = 26.60°$ (Xpert N. 01-0649), identified in the lamination waste, confirms the presence of alpha-quartz. The presence of silicon oxide (quartz) in the steel wastes was also reported by other authors (Grillo, Tenório, & Oliveira, 2013; Lima, Reis, & Borges, 2013). It may also be enhanced that rhodium was detected in the qualitative analysis of XRF but it was not registered by XRD, probably due to its low content in the wastes.

Figure 2 presents hydrogen consumption profile as a function of temperature for the MS, LA, LF and QC wastes. In fact, it provides a reduction peak between 250 and 280°C for all catalysts (see enlargement in Figure 2b). This peak has been attributed to the reduction of copper and rhodium oxide, reduced at low temperatures (Beyer, Emmerich, Chatziapostolou, & Kohler, 2011). The peak´s area revealed the following order: MS > LA > QC > BF.

In Figure 2, it may be noted that the reduction of iron oxide started around 500°C in the MS, LA and QC samples, although iron reduction is initiated at a higher temperature (615°C) in the BF sample, probably due to the interaction of iron oxide with other compounds in the sample.

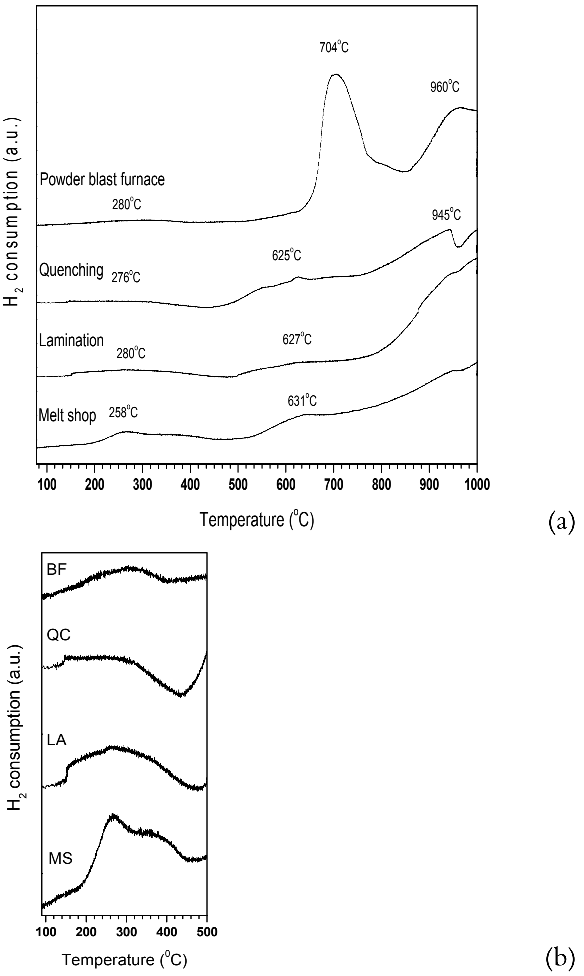

**Figure 2.** Results of (a) $H_2$-TPR analysis (b) enlargement of peaks at low temperatures.

In the reduction of iron oxide, hydrogen consumption is due to the reduction of $Fe^{3+}$ to $Fe^{2+}$ and from $Fe^{2+}$ to $Fe^0$. The calculation of molar ratio $H_2/Fe$ (hydrogen consumed per $Fe_2O_3$ mol in the sample) showed lower rates than 3, or rather, the partial reduction of iron oxide in the MS, LA, LF and QC catalysts (Table 3). As mentioned above, this result shows that other compounds in this waste may interfere in the iron oxide reduction.

**Table 3.** Hydrogen consumption obtained from $H_2$-TPR.

| Catalyst | $H_2$ consumption (mol) | $\frac{H_2\ mol}{Fe_2O_3\ mol}$ |
|---|---|---|
| Melt shop (MS) | $1.4 \times 10^{-4}$ | 2.09 |
| Lamination (LA) | $1.4 \times 10^{-4}$ | 1.45 |
| Quenching (QC) | $1.2 \times 10^{-4}$ | 1.34 |
| Powder blast furnace (BF) | $1.9 \times 10^{-4}$ | 2.91 |

Figure 3 shows $N_2O$ conversion as a function of reaction temperature. Or rather, conversion increases with increasing temperature for all the catalysts. Note that QC and BF catalysts presented similar conversions, even with different iron contents. Similar behavior is observed for MS and LA catalysts at temperatures lower than 200°C. However, above 200°C, MS catalyst has a higher conversion when compared to LA.

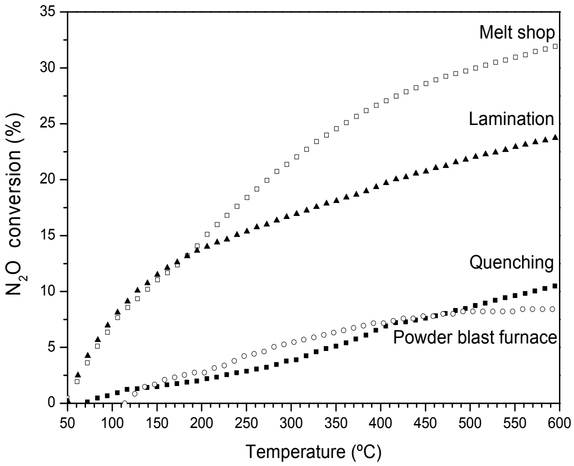

**Figure 3.** Results of evaluation of catalyst in the $N_2O$ reaction.

Figure 3 reveals that catalysts had the following conversion order: MS > LA > QC > BF. Note that conversion is related to the area of the first $H_2$-TPR peak due to copper and rhodium oxide (Table 4). Specialized literature shows that rhodium is highly active in $N_2O$ decomposition reaction (Zhao et al., 2010; Beyer, Emmerich, Chatziapostolou, & Kohler, 2011). Therefore, high rhodium content in catalyst MS has been associated with higher conversion (32.0%). The MS catalyst showed also a higher rate of nitrous oxide decomposition (12.2 mmol $N_2O\ s^{-1}\ g_{cat}^{-1}$) than other metallic oxides (1.3-8.8 mmol $N_2O\ s^{-1}\ g_{cat}^{-1}$; CuO, $Co_3O_4$, NiO, $Fe_2O_3$, $SnO_2$, $In_2O_3$, $Cr_2O_3$, $TiO_2$, $La_2O_3$, MgO and CaO) mentioned in the literature (Satsuma, Maeshima, Watanabe, & Hattori, 2001).

**Table 4.** Relationship between $N_2O$ conversion and $H_2$-TPR.

| Catalyst | (%) X $N_2O$ | Relative area from $H_2$-TPR[a] | (%) X $N_2O$ calculated [b] |
|---|---|---|---|
| Melt shop (MS) | 32.0 | 1.00 | 32.0 |
| Lamination (LA) | 23.8 | 0.69 | 22.1 |
| Quenching (QC) | 10.6 | 0.38 | 12.2 |
| Powder blast furnace (BF) | 8.4 | 0.33 | 10.6 |

[a] area first peak of the melt shop catalyst / area first peak of catalyst i. [b] $N_2O$ conversion of melt shop catalyst * relative area from catalyst i.

## Conclusion

XRD results from melt shop (MS), lamination (LA), quenching (QC) and powder blast furnace (LF) showed related peaks of hematite, magnetite, copper oxide, chromium oxide, calcium silicate and manganese oxide. $H_2$-TPR analyzes revealed a peak associated with rhodium oxide detected by XRF. Content of comparative rhodium oxide in the samples was MS > LA > QC > BF. $N_2O$ conversion increases in proportion to temperature increase for all catalysts. Catalytic activity followed the order: MS > LA > QC > BF, complying with rhodium oxide content. MS catalyst was the most promising for $N_2O$ decomposition reaction.

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