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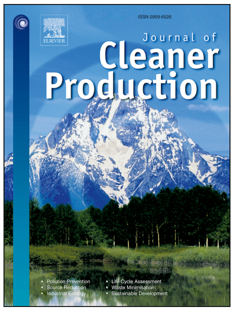

Microwave treatment of a hot mill sludge from the steel industry: *en route* to recycling an industrial waste

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ABSTRACT

Oily hot rolling mill (HRM) sludge containing a high percentage of iron oxides has been treated under microwave irradiation, and the products compared to hexane washed and thermal treated sludges. Metals present in the sludge act as a highly microwave-absorbent material, creating hot spots that trigger the stripping of the water and oils under air. The sludge looses 5 wt.% of water and volatiles under 5 min of microwave irradiation (1000 W at 2,450 MHz), which represents a similar reduction in weight as 4 h heating at 200 °C, but with savings in energy and time. Most importantly, after microwave irradiation, the material also shows an improvement in its rheological properties (free flowing and smaller particle size) and changes in its chemical composition. Microwaved samples are less oxidized than heated ones (lower Fe^{3+} content), which is an advantage recycling the sludge as a source of iron with lower oxidation state necessitates a lower coke:ore ratio for blast furnace operation.

Highlights

- Oily hot rolling mill (HRM) sludge treated with microwave radiation.
- Water and hydrocarbon content reduced by microwave treatment.
- Reduction of the iron oxidation state of the iron oxides after microwave treatment.

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organic residues. The recycling and recovery processes of the sludge are particularly challenging due to the presence of hydrocarbons with a low flash point in its composition (Park et al., 2002). High amounts of sludges are generated by the steel industry. One estimate suggesting that 0.9 ton of oily sludge is produced for every 1000 tons of rolling steel (Qin et al., 2015). Mill sludge cannot be recycled via sintering because of its high oil level (5 - 20%) and is normally treated as a landfill waste (Çamci et al., 2001; Martín et al., 2009). This waste product is creating an adverse impact on the environment due to the content of hazardous organic compounds especially if it is landfilled. The reuse of the iron content also is of economic necessity in reducing manufacturing costs within the steel industry in the UK, which is currently struggling to compete worldwide with cheap imports, cope with increasing energy bills, and increased legislated standards. The cost of manufacturing is a major contributor to the contraction in UK industry that is currently causing significant job losses and likely to impact much further with obvious and catastrophic effects on local communities that are heavily reliant on a single industrial employers in the area. By transforming or reusing hot rolling mill wastes, metals and mineral resources can be recovered and the environmental impact reduced with positive effects on UK manufacturing industry with regard to waste re-use and lower raw materials consumption leading to potentially lower costs and higher global competition.

Mill sludges with high oil content could be recycled via sintering, however, due to the high volatile organic compounds and dioxin emissions in exhaust fume systems, they are normally treated as landfill waste (Martín et al., 2009). Several approaches have been studied for the recovery of the metals and the removal of oils from the iron sludges (Park et al., 2002). Conventional methods for recycling HRM sludge include physiochemical and heating treatments. Heating methods are not generally used due to their high prices and low oil removal efficiency. Some researchers have proposed using a reduction followed by a magnetic separation step to recover the iron in the samples (Wang et al., 2014; Yu, 2014, Fard et al., 2016). Vacuum distillation followed by either an oxidizing roasting or a hydrogen reduction step have also been employed to obtain high purity ferric oxide powders (Liu et al., 2013a).

industrial wastes (Kingman et al., 2004; Kumar et al., 2010; Saito et al., 2011; Bobicki et al, 2014; Lam et al., 2015). The rheological behavior of different metallic slurries has been modified by using microwave energy (Sahoo et al., 2015), in addition microwave pyrolysis has been used as a disposal method for waste oil by using a bed of highly microwave-absorbent material (Lam et al., 2010). Pyrolysis of waste engine oil using a metallic pyrolysis char as a microwave-absorbent material has been reported (Lam et al., 2015). Rapid heating, decreased sintering temperatures and improved physical and mechanical properties have prompted us to investigate microwave energy for the synthesis and processing of a range of materials (Gomez et al., 2012; Landry et al., 1995), as well as the use of nanoparticles as “nano susceptors” (Gomez et al., 2015; Gomez et al., 2017; Gomez et al., 2016). Of particular interest with regard to the present study was the role of residual catalyst particles during the microwave purification of carbon nanotubes (Gomez et al., 2016). The potential of these iron oxide/iron nanoparticles to promote microwave heating suggested that similar effects could occur for HRM sludge.

In this study, we investigated the use of the microwaves to remove the water and reduce the amount of oils in industrial steel hot mill sludge. The goal is to recycle the material in order to reduce the environmental impact of landfilling it. Additionally, the cost of energy and raw materials is a major contributor to the contraction in UK manufacturing industry that is currently causing significant job losses and likely to impact much further with obvious and catastrophic effects on local communities that are heavily reliant on a single industrial employers in the area. The financial losses of UK industry as exemplified by the steel cannot be sustainable and the potential job losses and resulting society impact will be disastrous. Thus, the development of chemical processes that lower waste and allow for recycling of material must be a priority.

2. Experimental

2.1. Materials and Characterization

Hot rolling mill (HRM) sludge was provided by *Tata Steel* Strip Products UK *Port Talbot Works (Wales, UK)*. Hexane (≥95%) was obtained from Sigma Aldrich and was used as received. Thermogravimetric/differential thermal analysis (TG/DTA) was performed on a TA

°C/min. The exhaust gas from the TGA was monitored using a heated sample transfer line (350 °C) and a Thermoscientific i510 FTIR. Scans were taken approximately every 36 seconds for the duration of the TGA heating cycle. Scanning electron microscopy was performed using an Ultra-High Resolution FE-SEM S-4800 coupled with an energy dispersive X-ray analyzer (Inca X-ray analysis system, Oxford Instruments, Abingdon, United Kingdom) was used for the EDX analysis. Some of the samples were sputter coated with chromium to prevent charging. Fourier transform infrared (FTIR) measurements were carried out by Thermoscientific i510, recording spectra in the 400-4000 cm^{-1} region with 32 scans. For size determination 1 g of the samples was sieved at different mesh sizes: 200 µm (70 Mesh), 125 µm (120 Mesh) and 50 µm (270 Mesh) using 70/270 (VWR: 510-0708, 510-0718 and 510-0724) sieves and an automatic shaker (Endecotts: MIN200/23050). X-ray photoelectron spectroscopy (XPS) measurements were obtained using a PHI Quantera system with an aluminum X-ray source at 1486.7 eV operated at 15 kV. All samples were sputtered with Ar^+ ions for 1 min at 3 kV prior to recording measurements. A spectrum energy calibration was performed with respect to the C1s peak with binding energy set to 284.50 eV (NIST XPS database). The speciation and composition variation was obtained by recording the multiplex spectra for C1s, O1s, and Fe 2p3 elemental energy levels. A survey spectrum was measured at 140 eV pass energy, and individual peak spectra regions recorded at 26 eV. Data was analyzed with PHI MultiPak program (Version 9.6.1.7), using Gaussian-Lorentzian (80%) curves with Shirley background subtraction. Curves were fit using the peak position and FWHM values reported in literature (Gomez et al., 2016; Bhargava et al., 2007). X-ray diffraction (XRD) patterns were recorded on a Brüker d8 DISCOVER diffractometer with a Cu-K_α X-ray source (λ = 0.15418 nm and analyzed using Match 2 software. Phase identification was performed using DIFFRAC.EVA software. Rietveld quantitative phase analysis was carried out using Topas-Academic v4.1 software.

2.2. Microwave treatment

A domestic 1000 W microwave oven (Panasonic NN-CT579SBPQ) was used as the microwave in all the experiments. In all microwave reactions a sample of the sludge (500 mg) was placed in a glass vial and microwaved for 1 min periods at 1000 W power. A 50 mL

Table 1

Summary of sample abbreviations.

Sample name	Description
SL	As received sludge
SL-MW$_n$	*n* x 1 min of microwave irradiation
SL-200	200 °C for 4 h in air
SL-500	500 °C for 4 h in air
SL-HW	Washed with hexane and filtered

2.3. Thermal treatment

A sample of the as received sludge (500 mg) was placed in a crucible inside a tube furnace. The sample was then heated to 200 °C for 4 h under air atmosphere (SL-200). A similar process was used but heating to or 500 °C (SL-500).

2.4. Hexane extraction

A sample of the as received sludge (40 g) was stirred with hexane (90 mL) for 2 h. The mixture was then filtered and washed with hexane (2 x 10 mL). The dried sludge is retained for further analysis, while the hexane is removed from the eluent in a rotary evaporator and the remaining organic compounds isolated as an oil (SL-HW).

3. Results and discussion

3.1 HRM sludge

Hot mill sludge is a steel industry waste product formed by a concentrated mixture of solid and water. It generally contains metallic iron, iron oxides, traces of non-ferrous metals, alkaline compounds and oils from the rolling process (Martín et al., 2012). Previous studies suggested the composition of the sludge oil produced in a rolling steel process consists of 55% alkanes and alkenes and 22% carboxylic acids, ketones and aromatic hydrocarbons (Qin et al., 2012). Prior to treatment, the sample investigated herein was characterized to provide a baseline.

control of the rolls as well as the removal of any loose debris from the roll bite area is achieved by the addition of the lubricants. Table S1 (see ESI) provides a summary of the commercial names of the oils present in the sample and their characteristics. None of the components have a flash point below 200 °C; however, thermal degradation results in the formation of functional groups and lower flashpoint components, see below.

Fig. 1. A photograph of the as received HRM sludge sourced from Tata Steel Strip Products UK Port Talbot Works (Wales).

The thermogravimetric/differential thermal analysis (TG/DTA) of the as received HRM sludge is shown in Fig. 2. The sludge exhibits two weight loss steps, the first (5.6 wt.%) between 50-120 °C is consistent with water and possibly any volatile hydrocarbons, while the second (5.0%) occurs between 220-540 °C and is consistent with the characteristics of the original component oils. The slight mass increase above 500 °C is associated with oxidation of Fe(II) to Fe(III). A summary of the TG/DTA results is given in Table 2 along with those of the treated samples.

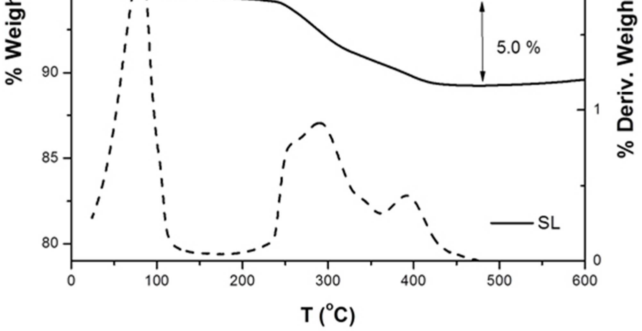


Fig. 2. The thermogravimetric analysis (solid line) and differential thermal analysis (dashed line) under N_2 atmosphere of the as received HRM sludge.

The FTIR spectrum (Fig. 3a) presents a broad band centered at 3300 cm^{-1} that corresponds to physisorbed water, peaks at 2920 and 2854 cm^{-1} due to aliphatic C-H, a large peak at 1630 cm^{-1} characteristic of the asymmetric stretching of carboxyl C=O groups, and 1450 cm^{-1} and 1372 cm^{-1} signals related to aliphatic C-H. A similar FTIR spectrum was obtained in a previous study on the recycling process of a rolling mill sludge based on a distillation step followed by either an oxidation or a reduction treatment (Liu et al., 2013a). This suggests that the sludge is representative of those from other steel works.

Table 2

Thermogravimetric analysis of as received HRM sludge before and after different treatments listed in Table 1.

Sample	Mass loss temp. (°C)	Wt% loss <200 °C (%)	Wt% loss 200-500 °C (%)	Residue @ 500 °C (%)
SL	81.5, 287.5, 395.2	5.6	5.0	89.4
SL-MW_1	296.5, 394.5	0.3	5.4	94.3
SL-MW_5	287.4, 396.8	0.3	4.0	95.6
SL-200	290.6, 376.8	0.2	5.5	94.3
SL-500	-	0.1	0.1	99.7
SL-HW	298	0.4	0.5	99.2

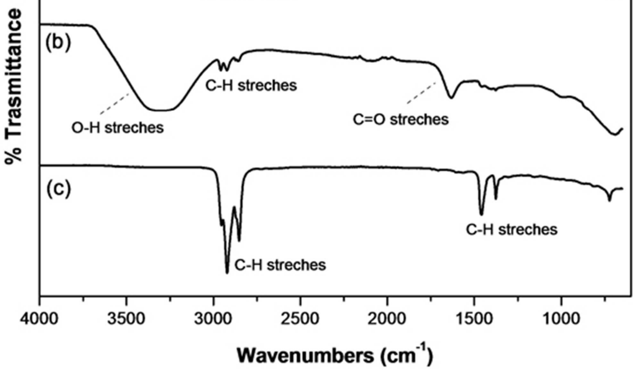


Fig. 3. FTIR spectrum of (a) the as received HRM sludge, (b) the solid residue after hexane extraction (SL-HW) and (c) the recovered organic compounds.

The chemical composition of the surface of the HRM sludge has been analyzed by XPS (Fig. S2). It should be noted that as a high vacuum technique, the sample had to be partially "dried" under vacuum before it could be placed in the chamber, thus the analysis of O (from H_2O) and C (from volatile organics) are lower than actually present; however, the objective was the determination of the Fe oxidation state. The high resolution XPS of the Fe $2p_{3/2}$ peak (Fig. 4a) suggest that Fe(III) represents the dominant oxidation state.

3.2 Treatment of HRM sludge

As previously noted, the oils in the sludge are composed mostly of hydrocarbons (Qin et al., 2015), which are non-polarizable molecules and therefore should not absorb microwaves. In order to determine both the effects of thermal and microwave treatment on the iron oxide component, the hydrocarbon material was extracted using hexane. As may be seen from the FTIR spectrum (Fig. 3b) of the solid residue after hexane washing (SL-HW), there is a significant decrease in the C-H and C-C stretches. The C=O band appears to be retained (along with the H_2O peak), suggesting that hexane washing does not remove functionalized organics. As expected, the FTIR of the organics extracted (see Fig. 3c) shows the converse signals, i.e., bands at 2923 and 2845 cm^{-1} (C-H), and also at 1460 and 1374 cm^{-1} (C-C).

TG/DTA of SL-HW shows small mass losses in both temperature ranges (Fig. 5a) due to incomplete extraction of the oils; however the mass increase due to Fe(II) oxidation (c.f. Fig. 1) is unchanged, confirming that the solvent extraction has no effect on the iron oxide expected by comparison of Fig. 2. The exhaust gas shows alkyl groups in the FTIR spectra (Fig. 5c).

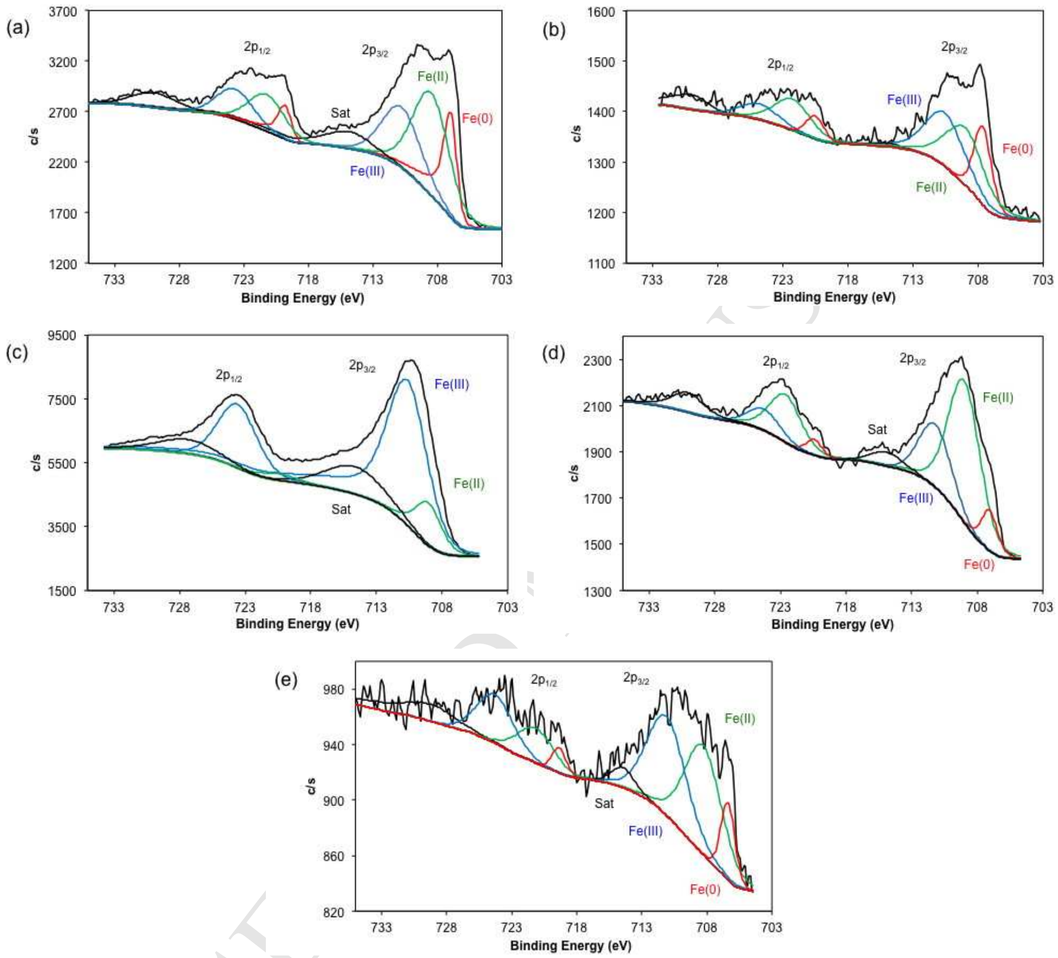
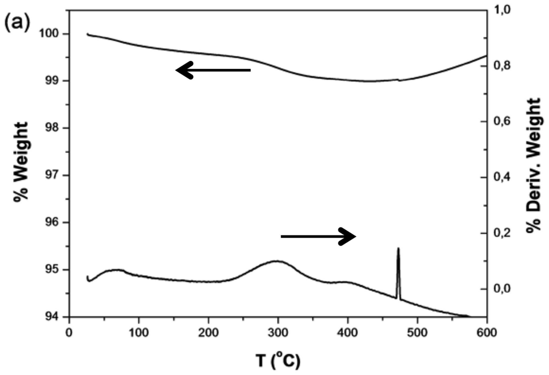


Fig. 4. High resolution Fe 2p XPS peaks of (a) the as received HRM sludge (SL), (b) SL-200, (c) SL-500, (d) SL-MW$_1$, and (e) SL-MW$_5$ samples.



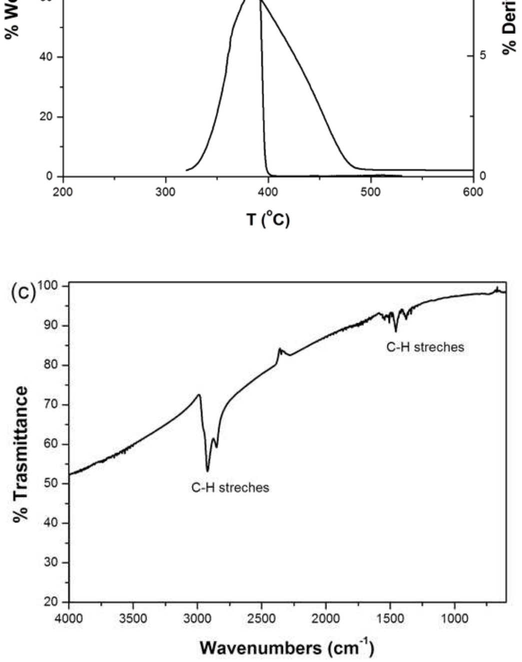


Fig. 4. (a) Thermogravimetric analysis and differential thermal analysis of (a) SL-HW and (b) the oils extracted by the hexane washing. Both experiments are performed under N_2 atmosphere. The FTIR spectra of exhaust gas (c).

Sludge samples have been treated by microwave irradiation with different times (SL-MW_n), and the resulting products characterized by TG/DTA, FTIR, SEM, EDS, XPS, and XRD. The position of the two steps in the TGA of the as received HRM sludge (Fig. 2) defined the choice of 200 °C and 500 °C for the thermal treatment (SL-200 and SL-500, respectively) as comparison with the microwave treatments.

TG/DTA results of the thermal and microwave treated samples (Fig. 6 and Table 2) show that none of the samples exhibit significant weight loss below 200 °C, consistent with the removal of water. This is confirmed from the FTIR spectra (Fig. 7), where SL-200 and SL-500 show no O-H band, while that observed for SL-MW_1 is significantly reduced as compared to SL. The O-H band is further reduced in SL-MW_5 as compared to SL-MW_1.

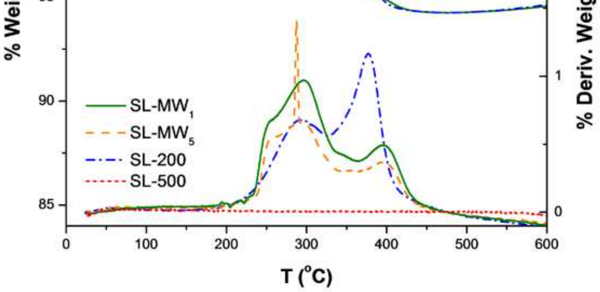


Fig. 6. The thermogravimetric analysis (upper lines) and differential thermal analysis (lower lines) in air of HRM sludge after microwave and thermal treatments.

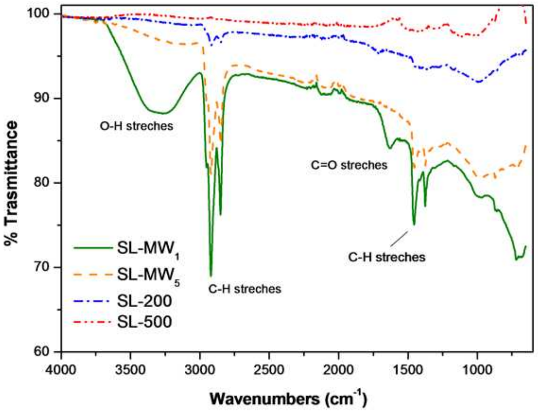


Fig. 7. FTIR spectra of HRM sludge after microwave and thermal treatments.

As expected, the SL-500 sample showed no mass loss due to either H_2O or hydrocarbon oils (Fig. 6), and is confirmed by the FTIR. In addition, no mass increase is observed, suggesting minimal oxidation of Fe(II) containing oxides in the TGA, i.e., the sample is pre-oxidized. While SL-200 shows no mass loss associated with H_2O, there is a mass loss 200-500 °C associated with the presence of the oils (c.f. the FTIR in Fig. 7), and the mass increase above 450 °C is also observed. The FTIR spectra of SL-MW$_1$ and SL-MW$_5$ show decreasing bands due to the hydrocarbon (Fig. 7), consistent with the TGA results. It is interesting that SL-MW$_5$ shows residual C-H and C-C bands, but no C=O band. The latter is also decreased in SL-MW$_1$ relative to the C-C bands.

EDX analysis results (Table 3) show a similar carbon atomic % for SL-200, SL-MW$_5$ and SL-MW$_1$ while SL-500 shows a significant reduction. These values are consistent with the were investigated by X-ray diffraction. As seen in Fig 8, the HRM sludge (SL) diffractogram shows peaks that correspond to three types of iron oxides: wüstite (FeO, COD 9006636), hematite (α-Fe_2O_3, COD 9000139) and magnetite (Fe_3O_4, COD1526955). Generally, the chemical composition of the mill scale varies according to the type of steel produced and the process used. Maghemite (Fe_2O_3) and pure iron (Fe) were identified to be the most abundant iron phases from a cold rolling mill sludge (Liu et al., 2013b), while others have reported a rolling mill scale comprised mainly of metallic iron and a mixture of the iron oxides wüstite (FeO), hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) (Martín et al., 2012). Our material appears closer to this latter composition.

Table 3

EDX analysis (atomic %) of HRM sludge samples after microwave and thermal treatments listed in Table 1. Each sample result is the average of three areas in the sample.

Sample	C	Fe	O	Si	Al	Ca
SL-MW_1	48.8 ± 0.5	22.2 ± 0.3	22.0 ± 0.3	4.8 ± 0.1	1.1 ± 0.1	0.6 ±0.1
SL-MW_5	37.4 ± 0.4	33.5 ± 0.3	24.2 ± 0.3	3.5 ± 0.1	0.7 ± 0.1	0.7 ±0.1
SL-200	40.6 ± 0.4	35.5 ± 0.3	21.8 ± 0.3	0.5 ± 0.1	0.6 ± 0.1	0.6 ±0.1
SL-500	34.8 ± 0.3	38.9 ± 0.3	23.8 ± 0.3	0.6 ± 0.1	0.9 ± 0.1	0.8 ±0.1

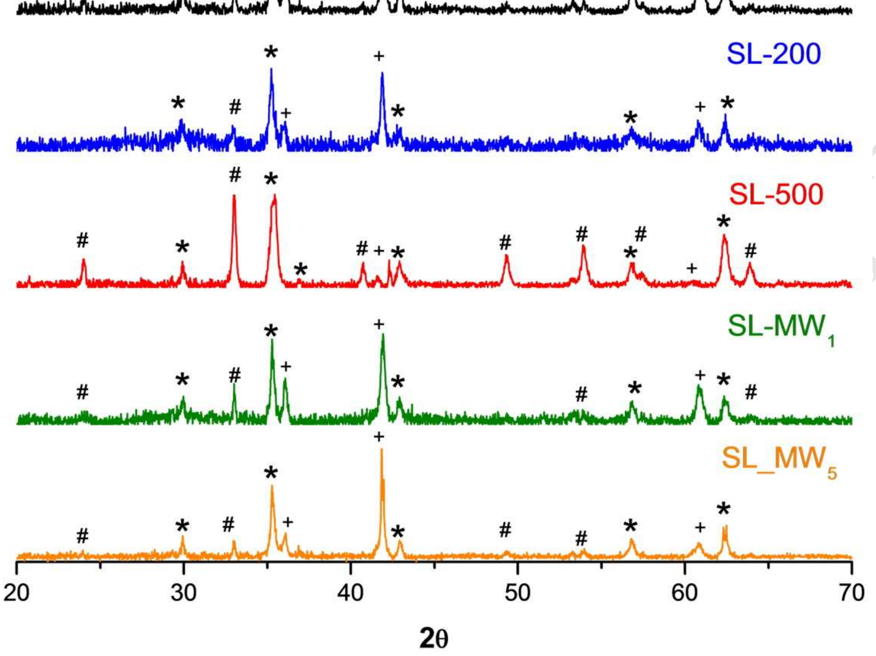


Fig. 8. XRD patterns of (a) SL, (b) SL-200, (c) SL-500, (d) SL-MW$_1$, and (e) SL-MW$_5$. Peaks are references for hematite (#, Fe_2O_3, COD 9000139), magnetite (*, Fe_3O_4, COD 1526955), and wüstite (+, FeO, COD 9006636).

Fig. 8 shows, upon thermal treatment to 200 °C, there is an expected reduction of the intensity of the wüstite (FeO) peaks occurring with a concomitant increase of the hematite (α-Fe_2O_3) peaks. This oxidation appears essentially complete at 500 °C, and given the kinetics for a magnetite to haematite transition (Monazam et al., 2014), explains why there is no appreciable mass gain above 550 °C in the TGA of SL-500. In contrast, microwave treatment of SL results in a similar phase composition as the original sludge. Using the Rietveld quantitative phase analysis (of the crystalline component) of the HRM sludge before and after various treatments is shown in Fig. 9 and Table 4, confirming the oxidation and reduction behavior.

Table 4

XRD Rietveld quantitative % phase analysis (HRM sludge samples after microwave and thermal treatments listed in Table 1.

Sample	Hematite	Magnetite	Wüstite	Iron	Goethite

SL-500	58	37	2	3	-

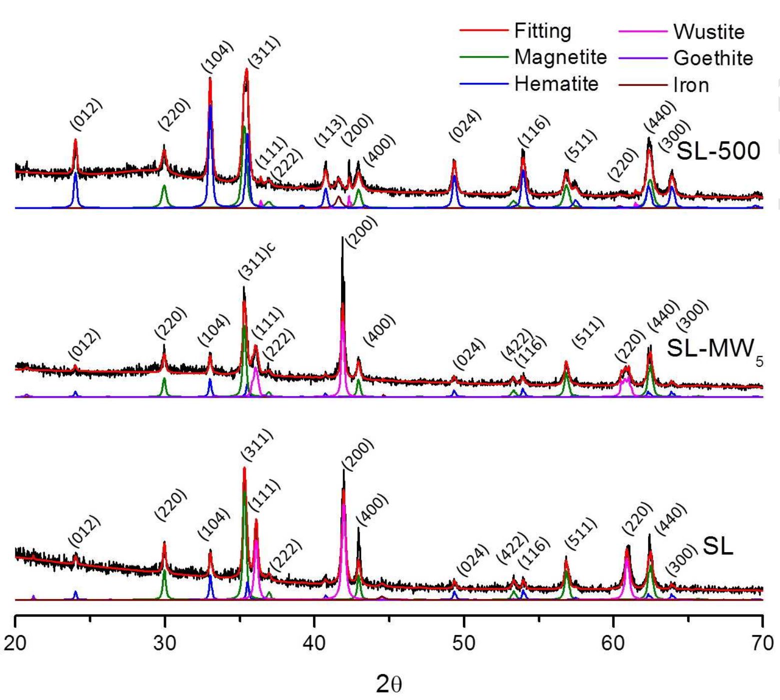


Fig. 9. Plot of crystalline phase composition of HRM sludge (SL) and compared to the various microwave and thermal treatments. Hematite (Fe_2O_3, COD 9000139), magnetite (Fe_3O_4, COD 1526955), wüstite (FeO, COD 9006636), goethite (α-FeO(OH), COD 9002158) and iron (Fe, COD 9000657) are observed.

The samples were studied by XPS in order to assess the iron state after heating and microwaving process (Table 5). XPS analysis showed spectral bands attributed to Fe $2p_{3/2}$, O 1s and C 1s (Fig S1). The analysis of the high-resolution Fe 2p signal on the samples by XPS (Fig 4) is in general agreement with the XRD data. In particular, the high resolution Fe 2p XPS spectrum of SL-500 shows no Fe^0 contribution (Fig. 4c), i.e., the average oxidation state of the iron oxides in the samples is increased by heating. It is also worth noting the relative ratio of Fe(II):Fe(III), see Table 4 and 5. Fig. 8 shows the dramatic reduction of the intensity of the wüstite (FeO) related peak while increasing the hematite (Fe_2O_3) ones after heating the sludge at 200 and 500 °C. According to the XRD and XPS results, microwave irradiation the solid–liquid suspension. The removal of water and/or the oils should have an effect on the agglomeration. As Fig. 1 shows, the particles in the as received sample are highly agglomerated. By comparison, after 5 min microwave treatment (SL-MW$_5$), the material kept a similar color and its particles are smaller in size (Fig. 11). Samples heated at 500 °C for 4 h under air show a color change from black-brownish to reddish related to increased oxidation of the iron in the sample (see below).

Table 5

Relative Fe(0), Fe(II) and Fe(III) content in HRM sludge samples after microwave and thermal treatment (listed in Table 1) as determined by XPS.

Sample	Fe(0)	Fe(II)	Fe(III)
SL	22.7	47.8	29.5
SL-MW$_1$	9.5	63.6	26.9
SL-MW$_5$	11.7	45.2	43.1
SL-200	23.1	38.8	38.0
SL-500	0	14.4	85.6

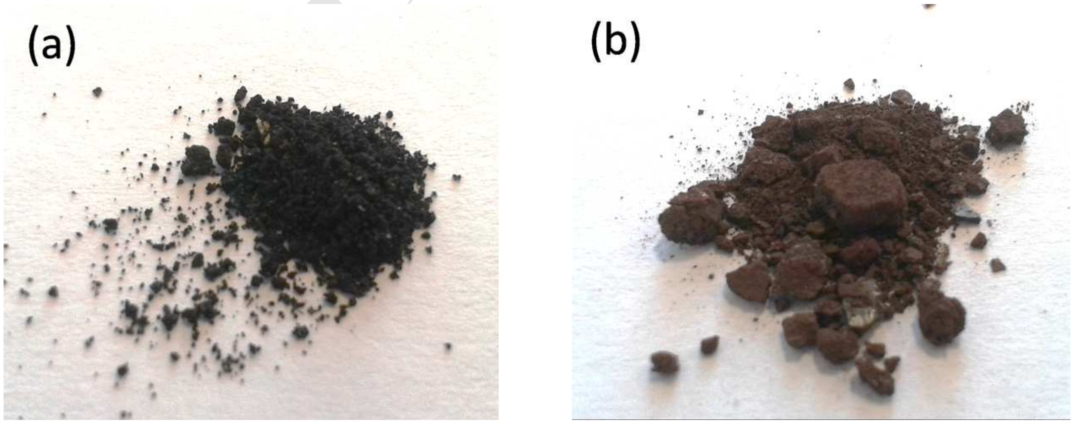


Fig. 10. Photographic images of HRM sludge after microwave and thermal treatment: (a) SL-MW$_5$ and (b) SL-500.

above the vaporization point of the oils (SL-500) dramatically changes the particle size distribution and, in particular, creates significant fines. Changes in rheological properties of iron ore have been observed previously; for example, it was found that microwave-treated iron ore have a lower density than that of untreated ore after grinding (Sahoo et al, 2015). In the present case, while SL-MW_1 samples reduce the hydrocarbon and H_2O content and make a free flowing solid, there is no significant decrease in the particle size, which would make subsequent processing simpler due to the problems of processing fine powders.

SEM results (Fig. S2 and S3, see ESI) show that the morphology of the mill scale powder is preferentially lamellar with heterogeneous surfaces formed basically by several micron size particles in agreement with sieving results. Interestingly, smoother surfaces have been found after microwave treatment of the samples.

Table 6

Sieving test results (%) for HRM sludge before and after different treatments listed in Table 1.[a]

Mesh size	Particle size (μm)	SL	SL-200	SL-500	SL-MW_1	SL-MW_5
70	212	99.9	98.0	60.0	99	88.4
120	125	-	2.0	16.5	1.0	7.1
270	53	-	-	18.4	-	3.1
Fines		-	-	5.2	-	1.4

[a] Some of the material can be lost in the sieving process due it´s stickiness.

If the consequence of the microwave irradiation was to simply heat the water, then the temperature would be limited ca. 100 °C. While this would explain the stripping of the more volatile hydrocarbon species, there are a series of changes consistent with higher temperatures. For example, steam stripping would not be responsible for changes in oxidation state, which suggest higher localized temperatures in the presence of a reducing species such as carbon. Microwave absorbing metals create hot points in the samples that explain this behavior. These hot points can reach high temperatures in a short time and generate sparks

4. Conclusions

Hot mill sludge is an iron oxide steel industry by-product with the ca. 10% content in water and oils resulting in a sticky solid that is difficult to manipulate. Furthermore, recycling becomes an issue because of the flammability of some of the components. Sludge samples have been treated by microwave irradiation, thermolysis, and washing with hexane in order to reduce their content in oils and improve their properties. Under microwaves, the rheological properties of the original sludge are improved. After just 5 min of microwaving, samples loose 5 wt.% of water and organic volatiles, a similar reduction to 4 h of conventional heating at 200 °C. FTIR results showed a reduction in the intensity of the O-H stretch and the alkyl groups, aromatic rings and carbonyl groups C=O signals related with the loss of water and organic material, respectively, in the microwaved samples. In addition, 10% of the particles have smaller sizes after being microwaved, related to an improvement of the rheological and transport properties of the sample.

Potentially, microwave energy is a faster and more efficient way for “drying” sludge than conventional heating, saving both energy and time. For potential scale-up of this process, there are, however, additional issues to be addressed, such as the cost of the microwave equipment versus traditional heating using natural gas or waste heat. The cost of any treatment versus the cost of storage and landfill must also be taken into account. A particular drawback is that the cost of the microwave equipment for scale treatment may result in a marginal economic case for implementation. Nevertheless, the most important observation is that microwaving the samples leads to less oxidation of the samples than heating them, which is an advantage in case a reduction step is added to recover the iron in the samples. The use of less coke per unit mass of raw material would benefit both production costs but also emissions.

Alternatively, microwaves can be used to trigger the oils pyrolysis. Sludge samples treated under air frequently catch fire, producing smoke (30 s under 1000 Watts). This behavior can be explained by the creation of hot points in the sample caused by microwave absorbing metals in the sludge. These hot points can reach high temperatures in a short time and generate sparks that can burn part of the organic compounds present in the sample.

sludge.

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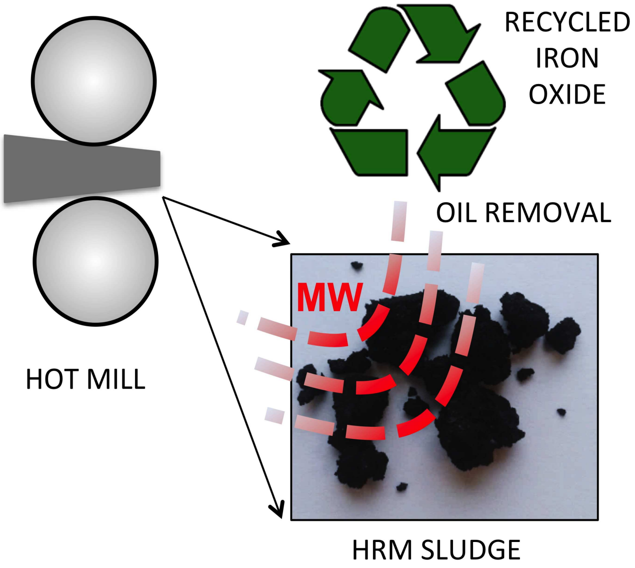
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