



Characterisation and classification of solid wastes coming from reductive acid leaching of low-grade manganiferous ore

Ida De Michelis^{a,*}, Francesco Ferella^{a,1}, Francesca Beolchini^{b,2},
Agostino Olivieri^a, Francesco Vegliò^{a,1}

^a University of L'Aquila, Department of Chemistry, Chemical Engineering and Materials, Monteluco di Roio, 67040 L'Aquila, Italy

^b Polytechnical University of Marche, Department of Marine Sciences, Via Breccie Bianche, 60131 Ancona, Italy

ARTICLE INFO

Article history:

Received 28 September 2007

Received in revised form 13 February 2008

Accepted 6 June 2008

Available online 17 June 2008

Keywords:

Leaching

Carbohydrates

Manganiferous ore

TCLP tests

ABSTRACT

The present work was focused on the acid leaching process for manganese extraction in reducing environment to low-grade manganiferous ore that comes from Central Italy. The aim of this study was to establish optimum leaching operating conditions to reduce treatment costs of waste or, even better, to allow a waste valorisation as raw materials for other applications. Consequently, the main focus of the work was the characterization and classification of the solid wastes coming from the process carried out at different operating conditions; at the same moment the effect of process parameters on Mn extraction was also analysed. The effect of particles size on the manganese extraction in reductive acid leaching process was investigated, by using lactose as reducing agent. Particle size did not show a large influence on the Mn extraction yields in the investigated process conditions. This aspect suggests the use of the leaching waste for civil and/or environmental application: use of leaching solid wastes like filling material is to be applied, for example, for environmental restoration. The classification of the solid wastes, according to the Italian Laws about Release Test (RT), has demonstrated that the solid waste produced by leaching can be classifiable as "hazardous special waste". An improvement of solid washing let to reduce the SO_4^{2-} and an appropriate treatment is necessary to reduce the dangerousness of these solids. Possible application of ore and waste as raw materials in the ceramic industry was demonstrated not to be feasible.

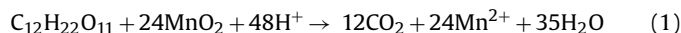
© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Low-grade ores, not treatable by means of conventional technologies (pyrometallurgical processes), represent a significant manganese source. Many hydrometallurgical processes are well documented in the literature aimed at manganese recovery from ores [1,2]. Manganese salts are generally obtained by acid leaching of ores containing the metal in its bivalent soluble form [3,4]. When manganese is present in the insoluble form Mn(IV), reducing agents are necessary to obtain the Mn(II) compounds. Many processes have been studied for manganese sulphate production by leaching with sulphuric acid in the presence of reducing agents [5–8].

These alternative processes include mixed methanol–sulphuric acid solution [9], coke [10], nonaqueous dimethyl sulphoxide [11], sulphuric acid and oxalic acid [12], iron(II) sulphate [13], and aqueous sulphur dioxide [5,14–16].

Previous works [17,18] have demonstrated the potential use of carbohydrates as reducing agent. This aspect has suggested the use of agro-industrial wastes, with the consequent development of an environmentally friendly process. By such process large manganese extraction yields were observed in a relatively short time by using either sucrose or glucose as reducing agents. It was demonstrated that the overall chemical reaction which takes place during the manganese dioxide dissolution in the presence of lactose may be described by the following reaction:



Different carbohydrates have been used in the leaching tests and a complex network of chemical reaction has been assumed by considering the carbohydrate chemistry in an acid media [6]. Several studies have been carried out to evaluate the best experimental conditions in terms of metal extraction yields. Many factors have been studied to check their effect on the manganese

* Corresponding author. Tel.: +39 0 862 434223; fax: +39 0 862 434203.

E-mail addresses: ida.demi@ing.univaq.it (I. De Michelis), ferellafrancesco@virgilio.it (F. Ferella), f.beolchini@univpm.it (F. Beolchini), agostino.olivieri@virgilio.it (A. Olivieri), veglio@ing.univaq.it (F. Vegliò).

¹ Tel.: +39 0 862 434223; fax: +39 0 862 434203.

² Tel.: +39 071 2204225; fax: +39 071 2204650.

Table 1

Experimental conditions and manganese extraction yields of leaching tests carried out by different size fraction of the investigated ore: pulp density 20%; temperature 90 °C; sulphuric acid concentration 1.5 M (stoichiometric excess 108%); lactose concentration 6 g/L (stoichiometric excess –42%), leaching time 5 h

Treatments No.	Initial MnSO ₄ (g/L)	Size fraction (mm)	Final MnEY (%)
1	0	0.18	49
2	0	0.6	51
3	0	1.2	57
4	0	10	58
5	40	0.18	50
6	40	0.6	50
7	40	1.2	48
8	40	10	55

extraction yields. These factors are: acid concentration; carbohydrate concentration; temperature; mixing. Previous works [6,17,18] have highlighted the considerable influence of temperature on the extraction yield, indicating a chemical control regime of the leaching process. Carbohydrate concentration and acid concentration have showed a positive effect on the Mn extraction yield; the hypothesis that more reactive species are formed during the first step of the leaching was also formulated [17,18]. Moreover, these works have demonstrated the technical feasibility of this acid and reductive leaching aimed at the recovery of manganese from different manganiferous ores [18].

A previous work [19] reported factorial experiments with the same manganiferous ore. From these data an empirical model was developed which lead to the following experimental conditions which maximize manganese extraction yields: ore concentration 30–35%, sulphuric acid stoichiometric excess 150–200% and lactose excess 0–10%.

In the present work, the main attention was directed to the solid wastes produced by the acid reductive leaching of low-grade manganiferous ores. In fact, the solid waste disposal considerably increases the total operating costs and it is fundamental to produce wastes not classifiable as “hazardous” (Directive 2003/33 Decree 13/3/2003 and D.M. 5/2/98) in order to have a “cost-effective” process. Furthermore, a significant reduction of total operating costs would be related to solid waste classification as “inert” waste, or, even better, to their valorisation and use as raw materials in other processes.

Firstly the effect of particle size on manganese extraction yield was investigated. This aspect is strictly linked to possible waste reuse applications: coarse particles in the solid waste would allow its reuse for civil/environmental uses. Then, different leaching operating conditions were investigated, with acid excess and ore concentration as factors considering both manganese extraction yields and wastes quality as responses. Therefore, solid wastes were analysed and characterized with the aim to verify the dump classification (norm UNI 10802)

Table 3

Experimental conditions and results of leaching tests carried out by different sulphuric acid concentration; size fraction 0.180 mm; temperature 90 °C; leaching time 5 h

Treatments No.	Pulp density (%)	Acid conc. (M)	Stoich.acid excess (%)	Lactose conc. (g/L)/Stoich. excess (%)	Final MnEY (%)	FeEY/Fe (g/L)
11	20	1.0	39	12/10	72	17%/1.37
12	20	1.5	108	12/10	61	18%/1.43
13	20	2.0	178	12/10	72	27%/2.18
14	20	3.0	317	12/10	73	32%/2.58
15	10	0.5	39	5.2/0	62	8%/0.31
16	10	0.75	108	5.2/0	84	12%/0.46
17	10	1.0	178	5.2/0	81	14%/0.56
18	10	1.5	317	5.2/0	75	16%/0.64
19	20	1.0	39	10.5/0	68	9%/0.71
20	20	1.5	108	10.5/0	78	11%/0.85
21	20	2.0	178	10.5/0	76	17%/1.37
22	20	3.0	317	10.5/0	76	26%/2.06

Table 2

Experimental conditions and results of leaching tests carried out by the investigated ore: size fraction 1 cm; pulp density 20%; temperature 90 °C; sulphuric acid concentration 3 M (stoichiometric excess 317%); lactose concentration 12 g/L (stoichiometric excess 17%), leaching time 5 h

Treatments No.	Initial MnSO ₄ (g/L)	Final MnEY (%)	Final FeEY (%)
9	0	85 ± 2	31 ± 1
10	40	78 ± 2	30 ± 1

as either “hazardous”, “not hazardous” or “inert”. The potential use in ceramic industry of both the ore and the leaching solid waste was also investigated in order to evaluate further reuse options.

2. Materials and methods

2.1. Ore

The manganiferous ore used in this work was collected from an Italian mine (mine in Northern Latium region, Italy). Samples were ground by RETSCH laboratory hammer mill and sieved.

2.2. Leaching procedures

The leaching tests were performed either in a screw flask (volume 300 mL) put in a thermostatic Dubnoff shaker (200 rpm) or in a thermostated stirred tank reactor (volume 5 L, 200 rpm). The ore was added to the lactose and sulphuric acid solution just when temperature selected for the leaching test was reached. Lactose and sulphuric acid concentrations were fixed according to operating conditions and evaluated as stoichiometric ratio to manganese amount in the ore, according to reaction (1). Periodically several amounts were sampled, centrifuged (5000 rpm), diluted in HNO₃ solution (pH 2) and analysed for manganese and iron determination. At the end of the process, the suspension was filtered (0.45 µm).

The operating conditions adopted during flask tests are reported in Tables 1–3.

All experiments were carried out at the same temperature (90 °C) and leaching time (5 h). Acid concentration and lactose concentration, in the treatments 9 and 10 (see Table 2), were doubled, 3 M and 12 g/L respectively, with respect to first series of treatments (1–8, see Table 1), whereas pulp density (20%) is the same in all of these experiments. To carry out treatments 9–10 (Table 2) and 11–22 (Table 3), two size fractions were selected, 1 cm and 180 µm, respectively.

Table 4 shows the operating condition adopted during the stirred tank reactor test.

Table 4
Operating conditions in stirred tank reactor leaching

Pulp density	30% (w/v)
Stoichiometric lactose excess	+10%
Stoichiometric acid excess	+100%
Temperature	80 °C
Mixing	~200 rpm
Particle size	180 µm

Some treatments (see Tables 1 and 2) were carried out with MnSO_4 in solution, the value of concentration (40 g/L) is limit value of out concentration of electrolytic cell in EMD production plant.

2.3. Solids characterization

Different granulometries were characterized by X-ray fluorescence (XRF) (Spectro Xepos) and XRD (Philips X-pert).

The ore's metals content was determined after an acid attack: 0.5 g of ore was suspended in 50 mL of sulphuric acid (3 M) with 1 g of oxalic acid (reducing agent) at 90 °C for 3 h; afterwards, the suspension was filtered and quantitatively recovered. The recovered solution was brought at volume of 100 mL, by deionised water, and analysed by atomic absorption spectrophotometry.

Baking tests were performed to check the possibility to use maniferous ore or leaching waste like raw materials or additives in ceramic production, as follows: solids were pressed to form disks (6 in total) that were fired in kiln at different temperatures (from 1160 to 1260 °C).

Release Tests (RTs) were performed in order to check the toxicity of solid waste and, consequently, to select the dump typology according to national laws. They were performed applying the procedures described in the norm UNI 10802 (D.Lgs. 13 January 2003, n.36: Italian actuation of directive 1999/31/CE about dump) and comparing the obtained results with reference values. The experimental procedure is the follow: the solid was put in a closed flask with deionised water in an S/L weight ratio 1:10, with constant mixing at room temperature and pressure. After 24 h the suspension was filtered (0.45 µm). The filtrate was analysed for anions determination (sulphates) and for the heavy metals determination (in the last case the collected samples were acidified by HNO_3 1 M at pH 2).

Table 5
Semi-quantitative elemental composition of the investigated ore for different particle size

% Element	Particle size			
	<1 cm	<1.2 mm	<0.6 mm	<180 µm
Mg	0.41	0.46	0.43	0.50
Al	5.56	5.81	5.39	5.94
Si	17.13	18.46	16.90	18.28
P	0.02	0.04	0.02	0.03
S	0.04	0.04	0.04	0.04
Cl	0.015	0.014	0.015	0.015
K	4.59	4.77	4.66	4.87
Ca	1.78	1.71	1.71	1.79
Ti	0.14	0.12	0.10	0.12
Cr	0.057	0.054	0.058	0.06
Mn	15.84	14.36	16.42	16.00
Fe	2.09	2.25	2.14	2.24
Co	0.016	0.032	0.019	0.018
Ni	0.017	0.013	0.014	0.014
Zn	0.04	0.03	0.04	0.04
Sr	0.08	0.08	0.09	0.09
Ba	0.80	0.99	0.99	0.94
As	<0.01	<0.01	<0.01	<0.01
Total	48.63	49.23	49.04	50.99

Table 6
Mineral composition by diffractometric analysis: particle size <1 cm

Element	Before size fraction
Leucite	KAlSi_2O_6
Analcime-O	$\text{Na}(\text{Si}_2\text{Al})\text{O}_6 \cdot \text{H}_2\text{O}$
Chabazite-Ca	$\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$
Cryptomelane-Q	$\text{KMn}_8\text{O}_{16}$
Rancieite	$(\text{Ca},\text{Mn})\text{Mn}_4\text{O}_9 \cdot 3\text{H}_2\text{O}$
Muscovite-1M	$\text{KAl}_2[(\text{OH})_2\text{AlSi}_3\text{O}_{10}]$
Quartz	SiO_2
Pyrolusite	MnO_2
Birnessite	$(\text{Na},\text{Ca},\text{K})(\text{Mn}^{4+},\text{Mn}^{3+})_2\text{O}_4 \cdot 1.5(\text{H}_2\text{O})$
Brownmillerite	$\text{Ca}_2(\text{Al},\text{Fe}^{3+})_2\text{O}_5$
Calcite	CaCO_3
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

"16 Days" Tests were performed in order to check the possibility to use the solid wastes as environmental restore or in civil work. They were made according to procedures described by the Italian D.M. 5th February 1998 (enclosure 3), as follows: the solid was put in a closed flask with deionised water in an S/L weight ratio 1:5, without mixing at room temperature and pressure. Periodically, at 2, 8, 24, 48, 72, 102, 168 and 384 h (16 days), the suspension was filtered (0.45 µm) and solids were re-suspended in deionised water. The filtrate was analysed for pH, Eh, anions (sulphates) and heavy metals determination (in the last case the collected samples were acidified by HNO_3 1 M at pH 2).

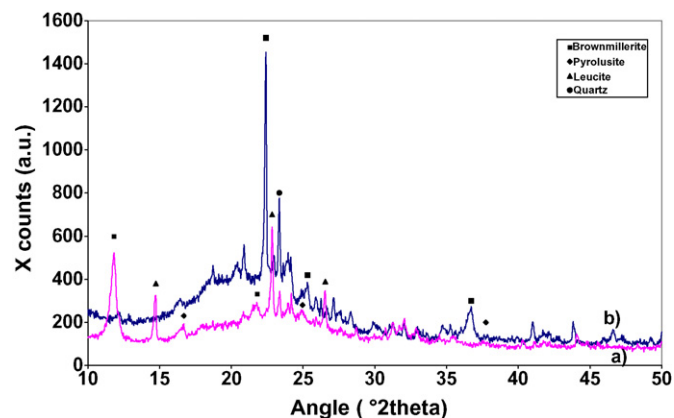
2.4. Analytical methods

Metals concentration (As, Ba, Cd, Co, Cr, Cu, Fe, Ni, Pb, Se, Zn, Mn) was detected by a Varian absorption spectrophotometer (Mod. Spectra AA-200).

SO_4^{2-} concentration was determined by DR LANGE LCK 153 test: sulphate ions react with barium chloride in aqueous solution to form barium sulphate, which is only sparingly soluble. The resulting turbidity is measured photometrically at wavelength of 430 nm.

NO_3^- concentration was determined by DR LANGE LCK 341 test: nitrites react with primary aromatic amines in acid solution to form diazonium salts. These combine with aromatic compounds that contain an amino group or a hydroxyl group to form intensively coloured azo dyes. The concentration is measured photometrically at wavelength of 515 nm.

Cl^- concentration was determined by DR LANGE LCK 311 test: during the reaction of chloride with mercury thiocyanate the slightly dissociated mercury(II) chloride is formed. Simultaneously an equivalent amount of thiocyanate ions set free, which react with iron(III) salts to form iron(III) thiocyanate. The concentration

**Fig. 1.** XRD (a) before and (b) after chemical leaching; principal phases.

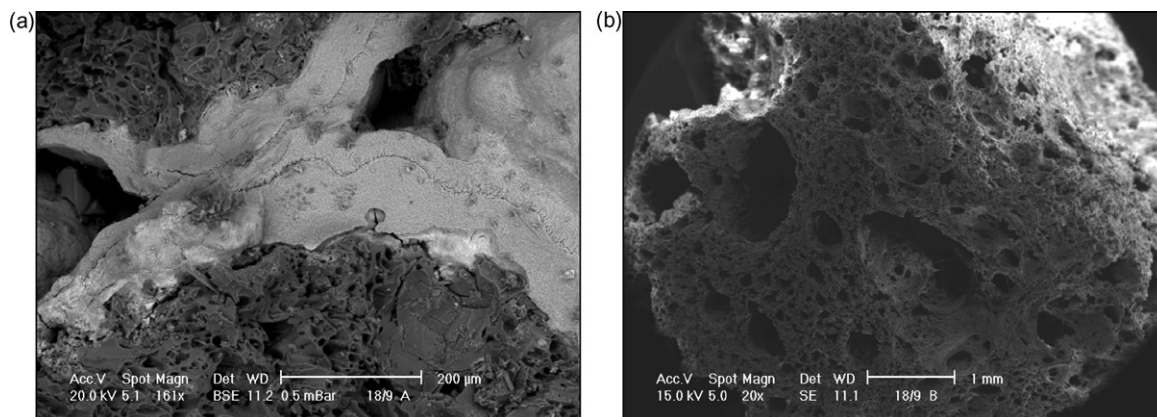


Fig. 2. SEM analysis of the ore (a) before and (b) after chemical leaching.

of this compound is measured photometrically at wavelength of 468 nm.

F^- concentration was determined by DR LANGE LCK 323 test: fluoride ions react with zirconium to form an uncoloured complex of zirconium fluoride. The red colour of the zirconium varnish disappears due to this reaction. The change of the intensities of the red colour is measured photometrically at wavelength of 588 nm.

COD was determined by DR LANGE LCK 514 test: oxidizable substances react with sulphuric acid–potassium dichromate solution in the presence of silver sulphate as a catalyst. Chloride is masked by mercury sulphate. The green coloration of Cr^{2+} is evaluated photometrically at wavelength of 610 nm.

SEM-EDS analysis was carried out by Philips SEM 505. Mineral characterisation was carried out by X-ray diffractometer (Philips X-Pert).

Elemental composition was determined by Spectro Xepos (XRF).

Measures of pH and Eh were carried out by Mettler Toledo MP220 pH-meter.

3. Experimental results

3.1. Leaching and solid waste characterization

The aim of these experiments was to find the best leaching conditions to achieve high manganese extraction yield and, at the same time, to obtain solid tailings that can be used like raw materials in other industrial sectors or, if this solution is not feasible, that can be collocated in dump as either not hazardous or, even better, inert material.

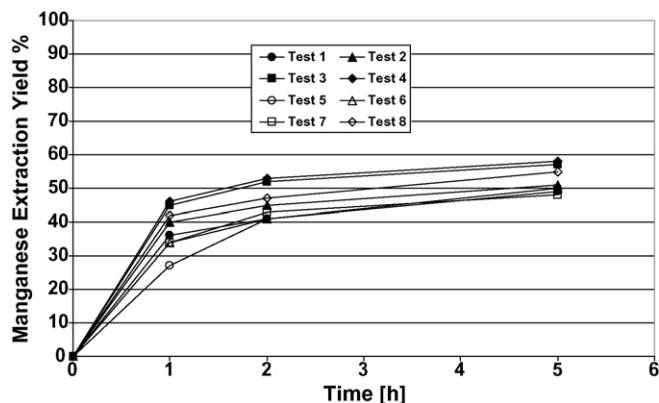


Fig. 3. Manganese extraction yield vs. time profiles for leaching treatments reported in Table 1.

3.1.1. Effect of particle size

Firstly, some tests were carried out to check the effect of particles size on manganese extraction yields. The interest in obtaining good extraction yields starting from coarse particles was connected to the potential use of the leaching solid wastes either as fill materials for civil works (for example: street construction) or for environmental restore, with a consequent reduction of the wastes cost management. In this case, the global process would be a “zero waste” process.

Table 1 shows experimental conditions and manganese extraction yields in shaken flasks leaching tests. Treatments 1–4 were carried out without $MnSO_4$ in solution whereas treatments 5–8 were carried out with $MnSO_4$ in solution to simulate the leaching of fresh ore either by acid solution coming from electrolytic cell, in which EMD (Electrolytic Manganese Dioxide) is produced or from another leaching step, in the case of a multistage crosscurrent operation (cross-leaching) [20] aimed at the reduction of acid consumption.

Table 5 shows the ore composition, for different granulometries, obtained by XRF as semi-quantitative results. It can be observed that differences among the determined compositions seem not to be significant. Quantitative analyses have also been performed by acid attack which gave a concentration of Mn and Fe of about 20% and 4%, respectively.

Table 6 shows the mineral composition (obtained by XRD) for one size fraction, other size were similar (they are not shown here). The solid residual produced during leaching treatments (Table 1, treatments 1–4) were also characterized by XRD. All samples show the same principal phases (Leucite, Brownmillerite, Quartz, Sadi-nite and Sillimanite), manganese minerals have not been found in the leaching waste. This might be due either to the amorphous phase that covers the manganese compound picks or to a manganese compounds concentration under instrument limit.

Fig. 1 shows one of the XRD-spectra of both manganese ore and leaching solid waste for the greatest particle size (leaching treatment No. 1 Table 1), other XRD-spectra were similar and they are not shown here. XRD-spectra show the presence in the ore of high percentage of amorphous phases that can cover picks of other compounds present in the solid; moreover, this amorphous component slightly rises after the chemical treatment, marking the changes in the phase present in the ore after the leaching treatment.

SEM analyses (Fig. 2) show ore morphology, that appears like porous structure covered by a gangue. At the end of leaching process (performed with the biggest particles size) the solid residual is composed essentially by a porous structure. This porous structure mainly consists of quartz (inert material), and it might be suitable for application as construction material in building trade. Further

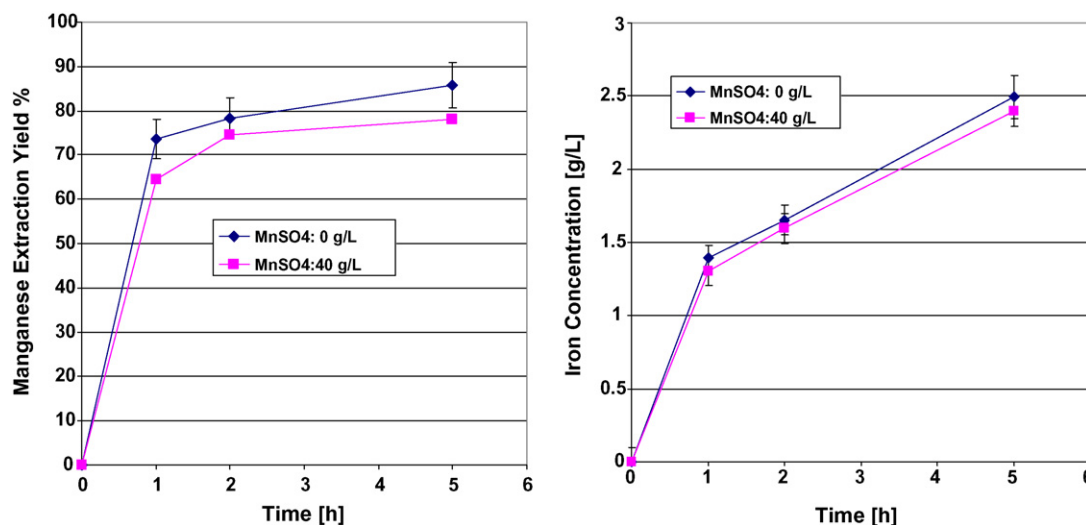


Fig. 4. Manganese extraction yield and iron concentration vs. time profiles in the treatment with and without MnSO_4 for the sample with particle size <1 cm (see Table 2).

tests aimed at toxicity characterization would be necessary to check the use of solid waste as construction materials. They are reported later, related to the solid waste coming from leaching test in a stirred tank reactor where higher manganese extraction yields have been achieved.

Data reported in Table 1 and in Fig. 3 confirm that manganese leaching does not significantly depend on particle size neither for the process kinetics nor for manganese extraction yields at equilibrium, in the investigated range. Initial Mn concentration is practically the same for each particle size (see Table 5). Furthermore, SEM analyses (Fig. 2) suggest that Mn is localized in a gangue that cover a porous structure, and its distribution is not uniform [21]: in fact the surface (after leaching) seemed like a pitting corrosion (presence of largest pores). Starting from this information, it is possible to conclude that the effective reactant surface (in which Mn is present) is the same for all particle sizes: this means that particle size is not expected to have any effect on Mn extraction yields. The slightly higher extraction yields obtained with the big size might be justified by the not so efficient mixing due to the equipment used (Dubnoff shaker) in the experiment. This equipment does not produce a perfect mixing: this bad condition has probably negative influence on smallest particle size than on the

biggest one. In fact the latter also shows an effect of floating due to this inner porous structure formed by quartz that improves the solid/liquid contact.

Consequently coarse ore might be used for leaching with consequent advantage of both filtration efficiency and potential reuse for civil application. So low manganese yields (<60%) are probably related to lactose concentration, that was under stoichiometric conditions (about –40%). This confirms the necessity to work in over-stoichiometric reagent condition, in agreement with results reported elsewhere [5,17,18]. Data also suggest that the presence of MnSO_4 in the leaching solution does not influence manganese extraction.

3.1.2. Effect of reagent excess

Considering these results, further leaching tests were carried out aimed both at achieving high manganese extraction yields and at producing wastes to be characterized by their toxicity. High acid excess and over-stoichiometric lactose concentration were chosen, with the greatest particle size. To check the reproducibility of the tests each treatment was replicated.

Table 2 shows experimental conditions and manganese extraction yield after 5 h of leaching treatment. Fig. 4 shows the process

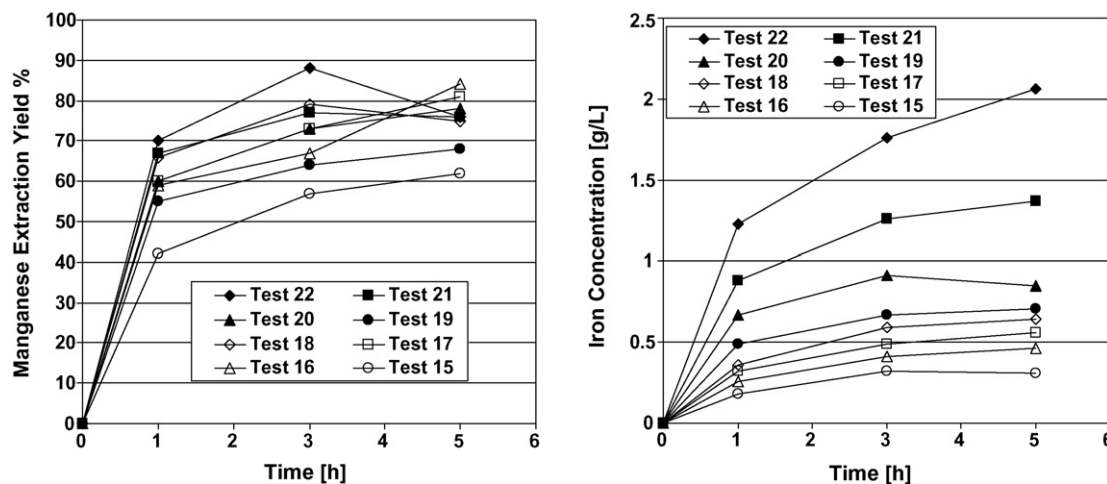


Fig. 5. Manganese extraction yield and iron concentration vs. time profiles for the treatment at different acid excess and pulp density for the sample with particle size <1 cm (see Table 3).

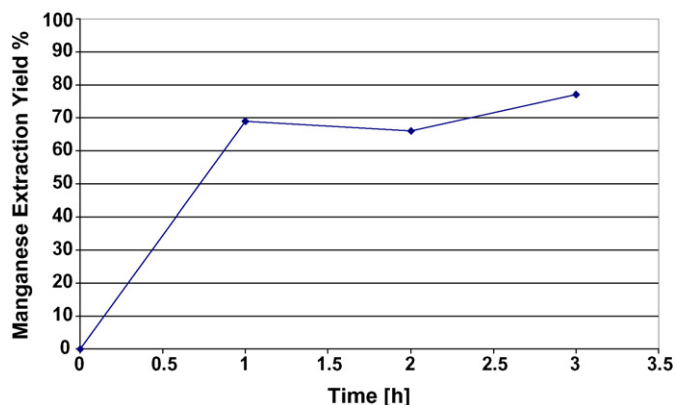


Fig. 6. Manganese extraction yield vs. time profiles in the stirred tank reactor (see Table 4).

kinetics (mean value of replicated tests and standard errors). Iron was also monitored (see Table 2 and Fig. 4), because it represents a contaminant of Mn products and its concentration is an important data for downstream operations [22,23].

These results confirm the necessity to carry out the leaching in over-stoichiometric condition, in order to achieve manganese extraction yield higher than 85%. The test carried out in the presence of $MnSO_4$ (treatment 10 in Table 2) show that Mn extraction yields is not significantly lower than the ones without $MnSO_4$ (treatment 9). Iron concentration trends are the same in all tests ($MnSO_4$ does not show any effect on iron dissolution).

Further tests were carried out at different acid excess in order to optimize the acid consumption. In fact, the amount of acid used during the process affects the raw material costs, especially it affects the consumption of base agent in the liquor leach purification steps. Pulp density was also considered as factor, Table 3 reports operating condition and Fig. 5 shows the concentration trend of treatments 15–22. These data show that it is possible to work at lowest acid excess, without any significantly loss in the Mn extraction.

A comparison of treatments 11–14 and 19–22 (Table 3) evidences that there is not effect of stoichiometric lactose excess, in the investigated range. Moreover, there is not any significant difference between the Mn extraction yields of treatments 15–18 and 19–22 (Table 3), achieved at different levels of ore concentration. Generally the Mn extraction yields decrease as ore concentration increases [24,25]; this effect is not much evident in these tests, so it is possible to conclude that ore concentration

does not have effect on manganese extraction, in the investigated range. The acid concentration does not significantly influence Mn extraction yields probably because all investigated levels are in a stoichiometric excess. On the other hand, iron concentration seems to increase with acid concentration (Table 3). This means that, at the lowest acid concentration manganese extraction yields is high, whereas the impurity of liquor leach due to iron is relatively low, with a consequent reduction of iron removal costs in the downstream operations aimed at liquor leach purification.

3.1.3. Process scale up

The last leaching test was performed in a stirred tank reactor, in order to check the process scale up. Operating conditions were chosen in according to previous works [19] and they are reported in Table 4.

Fig. 6 shows manganese extraction yields vs. time profile. The result obtained after 3 h of leaching was around 76%; this value was similar to extraction yield achieved in the flask tests under the same operating conditions (see Table 3 treatment 21). Therefore, both mixing and scale-up do not show any effect on the extraction yield.

The obtained leaching solid waste was also analysed by the test at 16 days (D.M. 5/2/98) to check the possibility to use this solid as fill materials or for environmental restore, and by RT (UNI 10802) to select the eventual dump typology (see Table 7).

RT was also carried out on the ore, that resulted classifiable as “inert” (data not reported here).

The law limits (Decree 5 Feb 1998 and Decree 13 Mar 2003) are reported in the last three columns of Table 7, the other columns show the results obtained for the waste sample. For the Italian test the following determinations are reported: the maximum value obtained during the eight measurements, the mean value and the sum value. This last value is compared with the law limits. These data show that the material is not adapt for environmental restore due to the arsenic and sulphate values.

Sulphate reduction and As remediation (either removal or immobilisation) represent a goal of future researches. Literature [26] shows that As(V) species would remain kinetically stable against reduction in the presence of either Mn or Fe, that appear like redox-active elements in the sludge. This means that probable As release (in the RT) can be decreased in presence of iron precipitates. These last compounds are produced in the downstream process. So, further research will be carried out to check the effect of leaching tailings and iron precipitates mixture on the RT results.

Table 7
Results of RT and DM 5/2/1998 tests on leaching solid waste (see Table 4)

pH	UNI 10802 (mg/L)	Italian test (5/2/1998) (mg/L)			Limit 5/2/1998 (mg/L)	Italian Dump Limit Directive 2003/33 e Decree 13/3/2003	
		Sum	Mean	Maximum		Inert (mg/L)	Not hazardous (mg/L)
	6.52						
As	0.136	1.26	0.157	0.438	0.05	0.05	0.2
Ba	0.039	0.905	0.113	0.219	1	2	10
Cd	<0.005	<0.005	<0.005	<0.005	0.005	0.004	0.1
Co	<0.01	<0.05	<0.01	<0.01	0.25		
Cr	<0.01	<0.05	<0.01	<0.01	0.05	0.05	1
Cu	<0.01	<0.05	<0.01	<0.01	0.05	0.2	5
Ni	<0.01	<0.01	<0.01	<0.01	0.01	0.04	1
Pb	<0.01	0.017	<0.01	0.01	0.05	0.05	1
Se	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.05
Zn	<0.01	<3	<0.015	<0.015	3	0.4	5
Mn	0.018	0.61	0.076	0.22			
NO_3^-	2.21	11.05	1.38	1.99	50		
Cl^-	0.89	4.74	0.59	1.21	200	80	1500
SO_4^{--}	123.7	640.5	80.06	100.6	250	100	2000
F^-	<0.05	<0.05	<0.05	<0.05	1.5	1	15
COD	<10	<10	<10	<10	30	50	80

Unfortunately, compounds present in the gangue do not permit also the use of leaching solid waste for building trade, in fact this solid residual cannot be classifiable as inert (see Table 7), unless further treatments were performed.

3.2. Tailings characterization for ceramic production

Both manganiferous ore and solid waste coming from leaching were also tested as possible raw materials for the ceramic industry.

The manganiferous ore was tested as additive in the preparation of gres sample (10%, w/w of ore). In order to check its performance, baking tests were performed and both shrinking and adsorption behaviour were monitored as a function of baking temperature. The obtained profiles have been compared with the expected ones, for gres samples with the proper characteristics (data not reported here). The ore answered negatively to baking tests (during these tests in the samples there was the formation of bubble). Sample with ore as additive (10%, w/w) in the preparation of the “gres” showed an anomalous behaviour, as concerns both shrinking and adsorption performances. In fact, the shrinking value at 1200 °C was just negative to indicate a material expansion (formation of bubble inside the material), whereas the adsorption did not show a decrease with temperature, until a value near zero was reached, as the control sample.

The leaching solid waste also resulted not to be applicable, since it contained still manganese that gives undesirable coloration. Therefore, such tests evidenced that both ore and solid waste cannot be used for the production of ceramic.

4. Conclusions

Main results of the present work are resumed in the following:

- Acid and lactose stoichiometric/excess are necessary to obtain good Mn extraction yields.
- Particle size, scale up and mixing do not significantly influence Mn extraction yields.
- MnSO₄ seems to reduce Mn extraction yields, however it is around 80%. So, it is possible to design a process flowsheet in which there is a cross-leaching (two leaching reactors in series) to optimize the process cost. In this process schema, the first reactor works with fresh acid solution (MnEY about 90%) and the second ones works with solution containing MnSO₄ coming from the first reactor (MnEY about 80%).
- It is possible to work at lowest acid excess (Mn extraction yields are practically the same in all tests) with a reduction of Fe dissolution and a consequently reduction of the operating cost connected to the purification process.
- Due to As and sulphate content (RT), solid wastes (leaching tailings) are classifiable as hazardous (high management cost), so it is impossible the use of these solids like raw material either for civil work or environmental restore. Moreover, neither the ore nor the leaching waste are suitable for the ceramic production.

Solid wastes declassification is very important to obtain an economical return on this kind of investment (production process of products with low value added). So, further research will be carried out with the aim to find the best process solution to reduce the hazardousness of the wastes (e.g.: optimal sequence of unit operation;

declassification of wastes by specific treatments; washing of solid wastes to remove the residual liquor leach).

Acknowledgements

The authors would like to thank Mr. Marcello Centofanti, Mrs. Lia Mosca and Mrs. Fabiola Ferrante for their precious technical assistance during the test works.

References

- [1] J.M.M. Paixão, J.C. Amaral, L.E. Memorial, L.R. Freitas, Sulphation of Carajas manganese ore, *Hydrometallurgy* 39 (1995) 215–222.
- [2] S.B. Kanungo, R.P. Das, Extraction of metals from manganese nodules of the Indian ocean by leaching in aqueous solutions of sulphur dioxide, *Hydrometallurgy* 20 (1998) 135–146.
- [3] K.N. Han, D.W. Fuerstenau, Acid leaching of ocean manganese nodules at elevated temperatures, *International Journal of Mineral Processing* 2 (1975) 163–171.
- [4] F.W.Y. Momade, Sulphuric acid leaching of the Ntusa manganese carbonate ore, *Hydrometallurgy* 49 (1996) 123–134.
- [5] F. Vegliò, L. Toro, Reductive leaching of a concentrate manganese dioxide ore in acid solution: stoichiometry and preliminary kinetic analysis, *International Journal of Mineral Processing* 40 (1994) 257–272.
- [6] F. Vegliò, M. Centofanti, F. Beolchini, S. Ubaldini, L. Toro, Manganese dioxide reductive leaching by sulphuric acid solutions containing carbohydrates, in: S. Atak, G. Onal, M.S. Celik (Eds.), *Innovation in Mineral and Coal Processing*, Balkema, Rotterdam, 1998, p. 457.
- [7] Y. Zhang, Q. Liu, C. Sun, Sulphuric acid leaching of ocean manganese nodules using phenols as reducing agents, *Mineral Engineering* 14 (2001) 525–537.
- [8] A.G. Kholmogorov, A.M. Zhyzhaev, U.S. Kononov, G.A. Moiseeva, G.L. Pashkov, The production of manganese dioxide from manganese ores of some deposits of the Siberian region of Russia, *Hydrometallurgy* 56 (2000) 1–11.
- [9] F.W.Y. Momade, Zs.G. Momade, Reductive leaching of manganese oxide ore in aqueous methanol–sulphuric acid medium, *Hydrometallurgy* 51 (1999) 103–113.
- [10] M. Pande, K.N. Gupta, Carbothermic reduction of manganese ore by low temperature carbonised coke, *NML Tech. J.* 30 (1988) 25–32.
- [11] P.R. Raison, S.G. Dixit, Leaching of MnO₂ with mixed non-aqueous solvent dimethyl sulfoxide, *J. Chem. Technol. Biotechnol.* 42 (1988) 167–182.
- [12] R.N. Sahoo, P.K. Naik, S.C. Das, Leaching of manganese ore using oxalic acid as reductant in sulphuric acid solution, *Hydrometallurgy* 62 (2001) 157–163.
- [13] S.C. Das, P.K. Sahoo, P.K. Rao, Extraction of manganese from low grade manganese ores by FeSO₄ leaching, *Hydrometallurgy* 8 (1982) 35–47.
- [14] C. Abbruzzese, Percolating leaching of manganese ores by aqueous sulphur dioxide, *Hydrometallurgy* 25 (1990) 85–97.
- [15] C. Abbruzzese, M.Y. Duarte, B. Paponetti, L. Toro, Biological and chemical processing of low grade ores, *Miner. Eng.* 3 (1990) 307–318.
- [16] P.K. Naik, L.B. Sukla, S.C. Das, Aqueous SO₂ leaching studies on Nishikhal manganese ore through factorial experiment, *Hydrometallurgy* 54 (2000) 217–228.
- [17] M. Trifoni, F. Vegliò, G. Taglieri, L. Toro, Acid leaching process by using glucose as reducing agent: a comparison among the efficiency of different kinds of manganiferous ores, *Minerals Engineering* 13 (2000) 217–221.
- [18] F. Vegliò, I. Volpe, M. Trifoni, L. Toro, Surface response methodology and preliminary process analysis in the study of manganiferous ores leaching by using whey or lactose in sulphuric acid solutions, *Ind. Eng. Chem. Res.* 39 (2000) 2947–2953.
- [19] F. Beolchini, A. Lancia, F. Pagnanelli, M. Centofanti, F. Vegliò, Reductive acid leaching of a manganiferous ore in the presence of whey and sulfuric acid, *The European Journal of Mineral Processing and Environmental Protection*, in press.
- [20] R.E. Treybal, *Mass Transfer Operation*, 3rd ed., McGraw-Hill, New York, 1980.
- [21] F. Vegliò, M. Trifoni, F. Pagnanelli, L. Toro, Shrinking core model with variable activation energy: a kinetic model of manganiferous ore leaching with sulphuric acid and lactose, *Hydrometallurgy* 60 (2001) 167–179.
- [22] Ullmann's *Encyclopedia of Industrial Chemistry*, Fifth Edition on CD-ROM, 1997.
- [23] F. Pagnanelli, M. Garavina, F. Vegliò, L. Toro, Preliminary screening of purification processes of liquor leach solutions obtained from reductive leaching of low-grade manganese ores, *Hydrometallurgy* 71 (2004) 319–327.
- [24] R. Acharya, M.K. Ghosh, S. Anand, R.P. Das, Leaching of metals from Indian ocean nodules in SO₂-H₂O-H₂SO₄-(NH₄)₂SO₄ medium, *Hydrometallurgy* 53 (1999) 169–175.
- [25] F. Vegliò, The optimization of manganese dioxide bioleaching media by fractional factorial experiments, *Process Biochemistry* 31 (8) (1996) 773–785.
- [26] S. Beauchemin, J.F. Fiset, T. MacKinnon, D. Hesterberg, Impact of a water cover on the stability of arsenic in a neutralization sludge. *Advances in mineral resources management and environmental geotechnology*, Hania 2004, Greece, pp. 519–524.