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Different applications of waste generated in reduction roasting – ammonia leaching of manganese nodules

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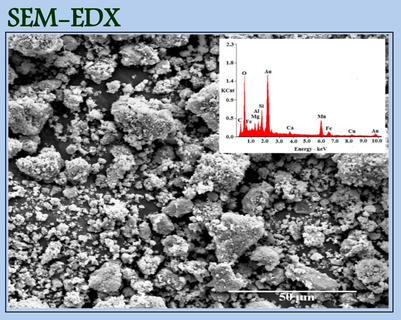
CSIR–NML, Jamshedpur has been engaged in technology development to recover valuable metals (Cu, Ni & Co) from manganese nodules (MN). Extensive R&D work led to development of a MN processing route based on reduction roast – ammonia leaching – solvent extraction (SX) – electrowining (EW). This process generates large amount of waste/residue (70% of the manganese nodule's weight) after selective leaching of Cu, Co and Ni, which may be considered hazardous, if untreated, due to its fineness and heavy metal contents. Being a powdery material manganese nodule residue posses high surface area. In addition, after leaching, entire manganese content end up in the residue. Keeping these in view, studies for utilisation of leached manganese nodule residue (MNR) have been carried out in three different ways: i) as source of Mn, ii) as adsorbent and iii) as catalyst and their details are illustrated in this poster.

Characterisation of Manganese Nodule Residue (MNR)

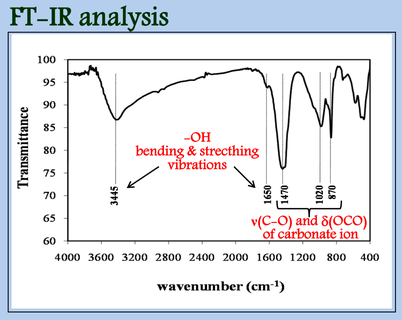
Chemical composition & other features

Element/radical	Wt.-%
Mn(Total)	26.11
Mn^{2+}	13.71
Mn^{3+}	4.92
Mn^{4+}	7.22
Fe	10.19
SiO_2	16.44
Al_2O_3	3.54
CaO	0.36
MgO	4.40
Co	0.039
Ni	0.05
Cu	0.13
Moisture	6.18
LOI	17.01
Surface area (m^2g^{-1})	66.70
Pore volume (cc g^{-1})	0.156
Pore dia.meter (Å)	37.6
pH_{pzc}	6.5
Mean particle size D_{50} (µm)	11.38

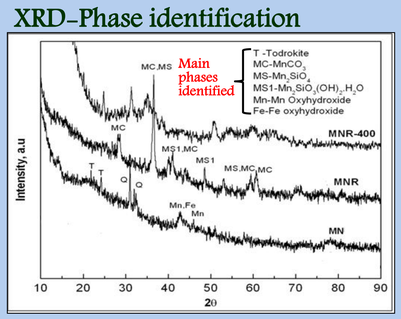
SEM–EDX



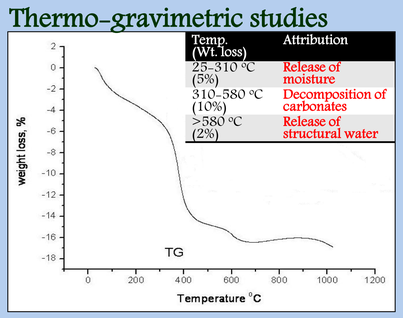
FT–IR analysis



XRD–Phase identification



Thermo–gravimetric studies



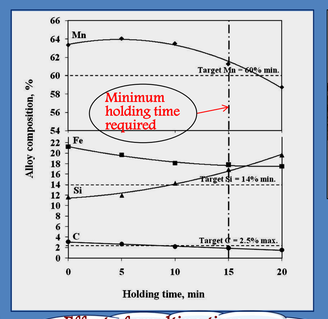
- MNR is very fine, Mn rich material with irregular particle having high surface area.
- Characterisation studies (XRD, FTIR & TGA) identified Mn carbonate and silicates as major constituents of MNR.

Mn Recovery by smelting

Smelted in a 50 kVA electric arc furnace to recover Mn as value added material : ferrosilicomanganese alloy

CHARGE MIX prepared by blending of raw materials in different ratios

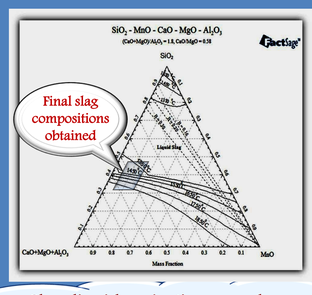
Smelting of CHARGE MIX



Effect of smelting time on alloy composition

Ferrosilicomanganese (FeSiMn) alloy

Slag



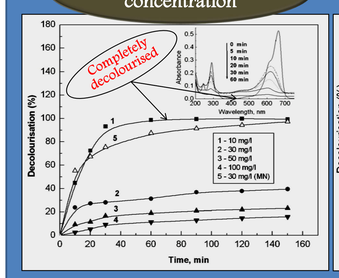
Slag–liquid projection: pseudo–ternary slag ($CaO+MgO+Al_2O_3$)–SiO_2–MnO

- ✓ Ferrosilicomanganese composition conforming to Si16Mn63 grade (IS1470,1990): Mn=60-65%, Si=14-17%, $S=0.03_{max}$, $P=0.3_{max}$, Produced.
- ✓ The optimum blending ratio between the MNR and Mn ore is found to be 1:0.6.
- ✓ Optimum conditions (Mn recovery , 77%):
  Charge mix having Mn/Fe ≥ 3.5,
  Mn/Si ≥2.5,
  B ($CaO+MgO/SiO_2$)= 0.2,
  R ($CaO+MgO/Al_2O_3$)=1.8,
  Holding time of 15 min
  at 1600±50 °C
- ✓ 4%(w/w) CaF_2 addition to melt enhances Mn recovery to ~87%

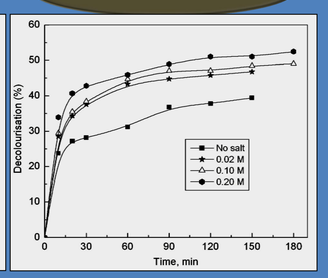
Catalyst

Assessed as catalyst for catalytic decolourisation of an organic pollutant: Methylene Blue (MB).

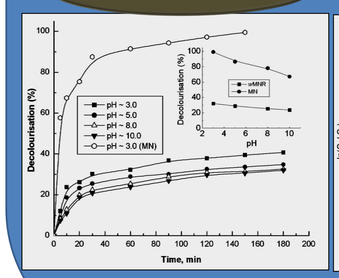
Effect if time and MB concentration



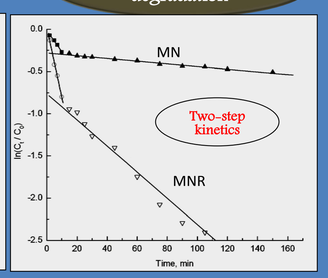
Effect salt addition



Effect of time and pH



Kinetics of MB degradation



- MNR is found effective towards decolourisation of MB.
- Extent of decolourisation depended on several factors and decreases with increase of pH values and initial MB concentration.
- The kinetic study shows a two-step consecutive decolourisation process; the first step is ~ 10 times higher than that of second step.
- Activity of MNR is enhanced in presence of H_2O_2 and NaCl at least at lower concentrations.
- Sulphate identified by ion-chromatography as major decolourisation/degradation product.
- Likely mechanism: Formation of MNR-MB surface complex → Electron transfer from MB to MNR → Release of product.

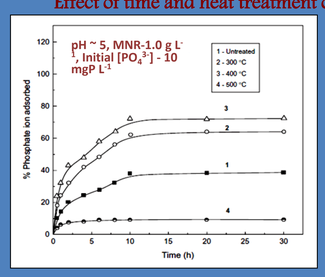
Adsorbent

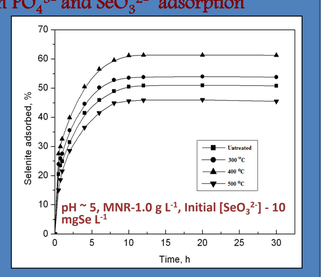
Evaluated as adsorbent for removal of pollutants: phosphate (PO_4^{3-}), selenite (SeO_3^{2-}) and cationic pollutants: copper (Cu^{2+}) and (Cd^{2+}) by batch adsorption studies

PO_4^{3-} and SeO_3^{2-}

- Adsorption follows: Freunlich isotherm & Pseudo first-order kinetics
- PO_4^{3-} and SeO_3^{2-} uptake increases with calcination of MNR up to 400 °C.
- Presence of Cl^-, NO_3^-, CO_3^{2-} and SO_4^{2-} up to 100 mgL^{-1} does not affect PO_4^{3-} and SeO_3^{2-} uptake.
- MNR regenerated by desorption of PO_4^{3-} and SeO_3^{2-} with eluent in alkaline pH.
- PO_4^{3-} loading capacity: 3.5 mgP/gMNR; 11.05 mgP/g activated MNR (400 °C)
- SeO_3^{2-} loading capacity: 9.5 mgSe/gMNR; 15.08 mgSe/g activated MNR (400 °C)

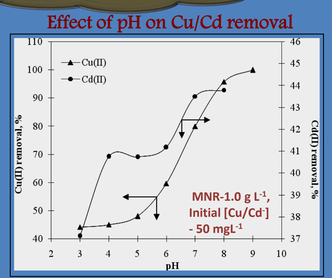
Effect of time and heat treatment on PO_4^{3-} and SeO_3^{2-} adsorption



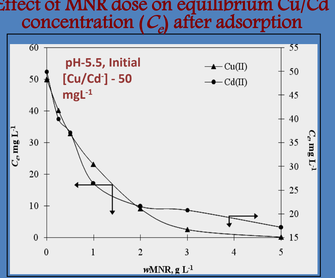


Cu^{2+} and Cd^{2+}

Effect of pH on Cu/Cd removal



Effect of MNR dose on equilibrium Cu/Cd concentration (C_e) after adsorption



- Adsorption follows: Langmuir isotherm & Pseudo second-order kinetics
- Adsorption equilibrium for Cu^{2+} and Cd^{2+} achieved in 240 min and 30 min respectively. Faster kinetics in case of Cd^{2+} uptake .
- Cu^{2+} and Cd^{2+} uptake increases with pH of solution.
- MNR regenerated by desorption of Cu^{2+} and Cd^{2+} with eluent at lower pH.
- Cu^{2+} loading capacity on MNR as function of temperature: 26.95 mg/g (30 °C); 32.36 mg/g (40 °C); 40.32 mg/g (50 °C).
- Cd^{2+} loading capacity on MNR as function of temperature: 32.26 mg/g (30 °C); 35.97 mg/g (40 °C); 38.17 mg/g (50 °C).

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