MICROWAVE CHARACTERISATION OF ZINC SLAG

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Executive Summary

1. Samples of zinc slag had been characterised from 1 – 12 GHz.
2. The characteristics show that there are two weak resonance peaks discovered over the whole band.
3. There is insignificant temperature effect on the loss factor as the sample temperature is raised to 200 °C

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1. Introduction

Recovering zinc from slags is an interesting application of microwave energy in waste minimisation and metal recovery.
The first phase of this work aims at characterising the microwave properties of zinc slag to see how the material will respond to microwave energy at different frequencies.
It is also of special interest in obtaining the theoretical amount of microwave energy which is required to heat zinc slag to 950 ^{0}C for industrial scale operations.

2. Material and Methods

a. Materials
Samples of zinc slag were provided. They were believed to contain a high proportion of zinc and a smaller proportion of lead. But the two metallic components were inseparable in the 'as received' state.

b. Physical properties
The specific density (g/cm3) and the specific heat (^{0}C/g) of the zinc slag were determined according to standard laboratory procedures.

c. Microwave properties
The microwave properties of zinc slag powder was determined using a specially designed probe to be used with an Automatic Network Analyser (ANA). The ANA is calibrated for measurements at each set frequency. The quantity measured is the reflected scattering parameter from the sample, which is then used, in a specially written program to compute the dielectric properties at each frequency. The frequencies used ranged from 1000 MHz to 12000 MHz.

d. Variation with temperature
Each sample of material was placed in a cavity of metallic heat block. Its temperature was slowly raised. The dielectric properties were measured at two frequencies: 922 MHz and 2450 MHz. The temperature of the heat block was raised to 200 ^{0}C and was cooled to ambient temperature.

3. Results

a. Microwave Dielectric Properties

Over the frequency range from 1 GHz to 12 GHz, the average dielectric constant and the average dielectric loss factor do not display any sharp resonances with frequency (Fig.1/ and summarised in Table 1). There are some fluctuations in the dielectric constant, which may be due to the size of the particle being coarse. The loss factor rises with frequency to display weak peaks at 5 GHz and 8GHz.

b. Penetration depth

The penetration depth (mm) is plotted in Fig.2.
The depth (mm) of 100 mm is possible at the lower frequency end of the spectrum. Bigger depth is possible with multiple sources using Dr. V.N.Tran's proven patent.

c. Resonant effect

There are two weak resonance peaks at 5 GHz and 8GHz. They have no practical significance (Fig.1).

d. Rate of power absorption

Fig.3 shows the rate of power absorption with frequency. The power absorption increases with frequency. For shallow penetration depth, the higher frequency has the advantage in a higher rate of absorption, hence a faster temperature rise, hence a faster processing. But the volume is smaller.

e. Temperature effect

The temperature effect up to 200 ^{0}C was investigated at 922 MHz and 2450 MHz. The results are plotted in Fig.4 and Fig.5. Some interesting results were observed at 922 MHz. The dielectric constant reduces with temperature while the loss factor shows a clear peak at 100 ^{0}C. The consequence for the former effect is estimated to be a twofold increase in penetration depth with temperature. The significance of the latter may be residing on some phase change or release of volatile at 100 ^{0}C.
At 2450 MHz, the dielectric constant seems to rise a little while the loss factor remains fairly constant with a slight dip at 150 ^{0}C. The cause for the former may be due to some chemical change, which increases the electric polarisation and hence reduces the penetration depth. The dip in the latter may be due to some chemical change, which prevents the molecules from moving freely with the microwaves.

4. Microwave Power Estimate

4.1 Energy and power requirement.
From the physical and microwave properties of zinc slag, the energy of power requirements are calculated.
The energy required to raise one tonne of zinc slag from the ambient temperature of 20 °C to 950 °C in one hour is 434 kW or approximately 500 kW. The power requirement is for any frequency. The cost per Watt at 922 MHz is presently the cheapest.

4.2 Temperature rate rise
The temperature rate rise for zinc slag is shown in Table 1. At 12000 MHz the rate is 0.11 °C/sec and at 922 MHz is 0.03 °C/sec, while at 2450 MHz is 0.02 °C/sec.

4.3 Microwave generator cost
At 2450 MHz, the cost per kW is \$ 5,000; at 922 MHz the cost per kW is \$ 4,000.
The cost for generators to heat up one tonne of zinc slag to 950 °C at 922 MHz is 500 kW x 4K\$ = \$ 2.0 M.
If the initial temperature is 200 °C, the power requirement is about 350 kW at an approximately cost of \$ 1.4 M.
4.4 Microwave generator at different throughput's:

a) 5 kg/hr: 3 kW generator: \$ 120,000
b) 50 kg/hr: 30 kW generator: \$ 400,000
c) 500 kg/hr: 175 kW generator: \$ 800,000

Programme Stage 3. Microwave-stimulated at 2450 MHz. Use standard fluidising pressures and microwave power to "temperature" relationships.

	Time (min)	850°C	900°C	950°C	1000°C
7.	x	A	B	C	D
8.	x + δx	E	F	G	H
9.	x + 2δx	I	J	K	L
10.	x + 3δx	M	N	O	P

Where A to P: (*i*) Slag + C, in N_2
(*ii*) Slag + C, in 20% CO/N_2
(*iii*) Slag, in 20% CO/N_2

Note that "fume end point" should lie between **9** and **10** .
Options D, H, L and P (at 1000°C) may not be needed. Also, other options may be cancelled. Possible experimental runs at temperatures below 850°C should institute a Stage 4 programme and are not proposed here.

Work Program

The work program of this contract refers to the first stage of a three-stage program discussed at a meeting between CSIRO and Tesla on 23rd October 2000. The objective of the overall program is the recovery of zinc from a blast furnace slag.

This first stage is concerned with determining the fluidization characteristics of the slag particles over a range of possible operating temperatures, fluidizing gas compositions and addition of a solid reductant. Particularly it is important to determine whether any sticky phases develop in the bed which could result in operational problems.

The program is defined as follows:

1. Determine the particle size distribution of a representative sample of the slag material supplied by Tesla. (Tesla is to provide approximately 50 kg of slag material, screened to -800 µm, and will be responsible for any costs associated with the return of samples, material accumulated during commissioning and any unused feed.)
2. Determine the apparent particle density and bulk density of the slag sample.
3. Determine the minimum fluidizing velocity of the slag sample in air at ambient conditions.
4. Conduct a Hazop/Hazid study of the proposed experimentation and complete a Health, Safety & Environment Assessment of the proposed work before any experimentation proceeds.
5. Modify and reconfigure an existing bubbling fluidized bed reactor rig to meet the requirements of this stage of the work program. The fluidized bed vessel is 50 mm ID expanding to 100 mm at the freeboard and is mounted in a gas-fired firebox.
6. CSIRO will provide brown coal char (Auschar) and determine by ambient condition fluidization tests the char particle size which mixes well with the much denser slag material. A bulk char sample will then be prepared by crushing and screening for use in the hot fluidization trials.
7. Select a superficial gas velocity, at operating conditions, which will be suitable for a mixed bed of slag and char particles (10 wt%).
8. Conduct twelve fluidization tests of up to 30 minutes duration each on approximately 0.35 kg portions of the slag sample as described in the following Table.

	Bed Material	Fluidizing Gas	Bed Temperature [°C]
Series 1	Slag	N_2	900°, 950° and 1000°
Series 2	Slag and crushed char	N_2	900°, 950° and 1000°
Series 3	Slag and crushed char	20 vol% CO in N_2	900°, 950° and 1000°
Series 4	Slag	20 vol% CO in N_2	900°, 950° and 1000°

During these parametric tests the fluidized bed temperature and differential pressure across the bed will be continuously monitored to try to identify any agglomeration and consequent defluidization of bed particles.

9. Samples of the final fluidized bed material of each of the 12 tests will be retained for analytical testing as required by Tesla. Note that any analytical charges will be additional item.

APPENDIX 2

RE: DIRECT ASSISTANCE AT Y-12 FOR TESLA SLAG

Dr. Hugo Huey of Micramics, traveled to Oak Ridge, TN on Aug. 29 to Sept. 1, 2000 to assist Stan Morrow in conducting and evaluating tests of slag material from Tesla. The work at Oak Ridge was supported by a direct assistance application by Micramics to examine the MW heating potential of slag provided by Tesla. An analysis of the data provided by Tesla and performed at Oak Ridge is provided below. Results of calculations on MW heating of slag based on general physics are also provided. Then estimates of the Zn production, capital costs and return on investment are given.

An initial heating test of ~180 g of slag powder in air at 2.45 GHz to 950 C without additives produced a broken alumina crucible with some molten slag spilling out the bottom. There was a large gap in the insulation for the 2-color optical pyrometer. The crucible outer wall temperature was taken for the temperature. There was a reddish (iron oxide?) crusty top remaining in the crucible, near the original position. There is a hollow cavity in the crucible with the crusty top. The melted slag was gray. The crucible probably broke during the cooling phase, which was just an abrupt turnoff. A clean white area was seen on the alumina fiberboard top cover. There may be small zinc bits on the alumina fiberboard and the crucible sides above the crust. Not a significant amount of Zn, if any, was collected on the alumina fiberboard cover.

Several other samples were then fired in alumina and SiC crucibles at 2.45 GHz in argon, nitrogen and normal air. All the alumina crucibles cracked. The chambers were not vacuum purged when argon or nitrogen was used. Plasma was observed in the Ar filled case. Dr. Huey did not witness the Ar case. The 'arcing' was periodic and probably coincides with the mode stirrer rotation. The mode stirrer is a three-sided reflector that may cause a significant periodic first pass heating. In Ar gas, plasma is easily generated by the lower ionization potential. It is possible that the plasma may be of the Zn vapor. The plasma should only change the results as a surface effect. The microwaves still penetrate and heat the slag from other directions. Nitrogen gas was used thereafter to avoid plasma arcs. The results appear to be more reddish material when just air was used. A quartz cover plate appears to pick up more metal and a light grayish powder when a nitrogen atmosphere is used.

Tests with carbon additives in nitrogen gas were tried. A small amount of vacuum was first tried. It produced significantly more metallic material, but a black oily material was also deposited on the quartz cover plate (and probably around the chamber). Char or charcoal was not immediately available.

Sugar (20 gm sucrose) was used and it produced the most amount of Zn-like material on the quartz. A reaction with the quartz also occurred. A significant amount of grayish ash covered the entire chamber.

A sample was heated in the 24 GHz system, but at a significantly slower rate. Only about 3.5 kW was used and the material reached 900 C. No cover material was available. It was heated in air. The result was a reddish powder throughout. No melting, no cracked crucible. It appears that the total slag reduced to this red powder. It would be interesting to know if there is any Zn left in it. It is likely that all the Zn is oxidized in a ZnO form in the reddish powder. The sample was bagged in 2 bags, one containing reddish powder from about the top ¼ and the 2nd mostly from the next ¼ in depth (to about ½).

A sample was heated at 915 MHz in a single mode traveling wave configuration. I was not able to witness it, but Dr. White had reported some plasma in air and a required 20-30 kW magnetron output to get about 1 kW absorbed power. The sample slag powder was placed in a pyrex beaker and heated in a WR975 standard waveguide. The beaker was small compared to the cross section of the waveguide. A calculation of the electric field strength incident on the sample is about 404 V/cm or 163 W/cm2 at 25 kW. Note at 2.45 GHz waveguide WR340, the equivalent incident power density (or electric field) would be yield a total power of only 3 kW, just because of the waveguide size at that frequency. In a chamber cavity the cavity Q would increase the electric field. So the high incident power at 915 MHz is not unusual. The pyrex beaker melted somewhat which is also not unexpected at 950 C. In consideration of the size of the sample compared to the rough estimates of penetration depth, the low coupling is not unexpected. To achieve good coupling and heating at 915 MHz would require a chamber furnace with at least a few kilograms of slag powder.

CALCULATIONS

Data from Tesla was provided. It included analyses of the slag and a microwave report by Prof. Tran of RMIT. A dielectric measurement by T. White at Oak Ridge Fusion Division was also conducted here. A separate critique and extended calculations are provided herein.

Microwave properties of slag powder were performed. The results of a powder measurement depends on a number of factors, including: powder size, distribution, filling factor, humidity, contact pressure, sample dimensions (especially at low frequency) and length of insertion and thickness. A solid slab with a smooth surface for contact would have been a better measurement. Thus both dielectric measurements do not agree. Both are suspect. No attempt was made to determine the intrinsic properties based on mixture theories and relative density.

For example, Tran: e'=4.3, e"=.4

while White: e'=7.8, e"=1.07 at 2.45 GHz

The values are quite different. Recommend measurements with solid slag, cut and polished to required dimensions for probe tests and cavity tests. Their measurements at the 1 GHz range and below are probably not thick enough since the penetration depth may be much larger than the sample. The actual heating of a powdered slag will depend somewhat on the effective dielectric constant. However, if the amount of powder is at least 1 tonne, then the effective density of the powder at the bottom is different from the top. Multiple measurements of this sort would be necessary to find a relevant empirical mixing rule.

The powder also has some magnetic bits. A moderate strength magnet only picked up a tiny fraction of the particles at Y-12, so the effective average magnetic permeability is probably small. There are probably some bits of free ferromagnetic material such as Fe, Ni or Co, but the sizes are very small and the total fraction is tiny. T. White's dielectric measurement assumed that the relative magnetic permeability is 1 (nonmagnetic). This was noted by Dr. White, but not by Dr. Tran. Separating the permeability may be difficult since the uniformity of the magnetic permeability is probably not good either. An effective dielectric constant and loss factor would suffice. Note at high enough temperatures, the materials will react, possibly removing the magnetic permeability. At temperatures above the Curie temperature, the remnant ferromagnetic permeability will cease. I would think that the chemical reactions such as oxidation, alloying, etc. would remove most of the magnetic permeability at high temperature.

Temperature dependence on dielectric properties are important, however, room temperature to 200 C yields a small range and questions of humidity and powder density will mask the measurements. A temperature range as large as possible would be better, also with a solid slag, not a powder.

Dr. Tran and Dr. White then calculate a penetration depth. No actual measurement was made. There is no agreement as expected. More information is needed here especially at 1 GHz and below.

Dr. Tran incorrectly calculates the Brewster angle. He used the loss factor as the second material dielectric constant. A measurement would have identified the error. Brewster angle is relatively insensitive to dielectric constant. Such a measurement would have to be performed carefully to get a precise dielectric constant confirmation.

Dr Tran's power absorption data appears to be calculated, since it is given for a wide frequency range. Thus the temperature rate given was probably calculated.

Dr Tran provides a specific heat capacity of 1.68 (j/g C probably) which would yield 0.40 cal/g-C. This value appears to be high, based on the weighted average value of the components and my experience with calculating heating of ceramics. This is a critical value for heating. It may be possible that phase transitions or chemical reactions may have affected the specific heat determination. I suggest a Differential Thermal Analysis (DTA) to identify some of the varying properties. If DTA can be accomplished up to 950 C, that would be very helpful.

Heating Calculations

I have performed heating calculations based on first physical principles. The purpose of such a calculation provides a basis for estimating the MW heating feasibility, efficiency, operating and capital costs. It also reveals several key factors affecting cost.

I will outline the calculations and then provide a few interesting results. The simple heating is based on an effective heat capacity (specific heat). Room temperature specific heat is often given. For most materials heat capacity will increase a bit at high temperature Tran's value of

0.4 cal/g-C is initially used, but 0.3 cal/g-C is felt to be more accurate. A few calculations with 0.4 are given below.

Tran calculates heating based on heat capacity, but all heating problems include heating of insulators, crucibles, supports, phase transitions, chemical reactions and cooling (blackbody, conduction and convection). An estimate of crucible, insulator size and mass, and factors for heat losses are made. Tran provides a density of 2.47 (g/cc probably), but this is the solid specific density. Assuming powder is less dense, a density of 2 g/cc is used to estimate crucible & insulator sizes. An estimate of 60 J/gm of Zn for heat of fusion is made, assuming all the 15% Zn undergoes this transition. A higher value may have to used for heat of fusion since at 950 outer crucible temperature, the slag melted in both the alumina and SiC crucibles. Other chemical reactions are suspected which may be endothermic and exothermic. The actual slag melting temperature is said to be ~1200 C. A side hole in a SiC crucible indicated the slag temperature for one 2.45 GHz test was equal or below the outer crucible temperature. Thereafter temperature was not measured directly with the slag at 2.45 GHz. A 24 GHz experiment with a direct 2-color pyrometer on the slag top at only 910 C, did not melt. It is possible that the internal slag temperature may have increased, while the outer crust temperature was less. Poor thermal contact between the slag crust and crucible may also yield a lower crucible temperature.

For BB temperature of 950 C, and an outer insulation temp of 275 C (a little high) are assumed, with a water cooled chamber temperature of 50 C. In the case of a fluidized bed, there is greater convection loss, but a recirculating heated air/gas will help minimize that. Heat loss is calculated at final equilibrated temperature for the entire time period. Then convection and conduction is estimated as a mere factor times BB loss. Specific thermal losses require a more detailed design, but the estimate should be close.

In any massive industrial process, there is heat recapture. Thermal recycling is estimated by a top off loss and a number of cycles. For example, 10 cycles would consist of one heat from room temperature and the rest at a 20% top off. The calculation then is only an average. But I can adjust it to handle the 100% and 20% specifically. Actually, we can 'preheat' the initial load in a variety of ways.

Time is a crucial factor for throughput and MW source power. A 1 hour time is used per metric ton (tonne) of slag.

Actual heating schedules start at low power and ramp up. This calculation assumes that the heating rate is constant (an average), so a linear ramp would have a peak power at twice the average power. A real heating profile is a ramp to a maximum power at about 1/2 time, held for awhile and decreased to gently reach the desired temperature with low overshoot. Thus a peak power of about 80% peak is more accurate to determine MW peak power requirements. A 77% microwave coupling efficiency is used.

Efficiency also depends on how the microwave couples to the material, impedance matching, microwave generation, and power supply efficiency. Thus cost for electrical operation should include these factors. A $0.10 USD/kW-hr is used to calculate the cost of electricity. This is easily scaled for other electrical cost. Costs (USD) for heat recirculation, cooling systems, material handling, material pre- and post-processing, and labor are not included.

Table 1

CASE:	A	B	C	D	E	F	
sp ht	0.4	0.3	0.3	0.3	0.3	0.3	
temp	950					850	
outer temp	275					215	
cruc divide	4				5	5	
time (hr)	1		1	1	1	1	
topoff	0.2					0.17	
# cycles	10		1	1000	10	22	
load ht	4.36E+08	3.27E+08	1.17E+09	2.35E+08	3.27E+08	2.07E+08	
cruc ht	5.40E+07		1.93E+08	3.87E+07	4.32E+07	2.73E+07	
phase ht	1.70E+07		1.70E+07	1.70E+07		1.70E+07	
tot ht loss	1.84E+08		1.84E+08	1.84E+08	1.48E+08	8.53E+07	
tot heat(J)	6.92E+08	5.83E+08	1.56E+09	4.75E+08	5.35E+08	3.36E+08	
est pk MW	399313	336336	902263	274084	308812	194096	
2.45 $e/load	$43.82	$36.90	$122.37	$30.07	$33.88	$21.30	
915 $e/load	$34.62	$29.16	$96.68	$23.76	$26.77	$16.83	
$/915sys	1597252	1345344	3609052	1096336	1235248	776384	@$4/W

Case A shows heating for a sp ht of 0.4 cal/g which may be high. With recirculation at 10 cycles, the calculation is an average of the single full heat and 9 with recirculation. Case B (and thereafter) reduces the sp heat to 0.3 cal/g. Case C shows without heat recirculation while Case D assumes high recirculation to model an individual run with recirculation. The crucible and supports are estimated so case E reduces the crucible load by 20%. Case F is a wishful highly efficient condition at low temperature. System cost at $4/W was used to estimate the MW system (source and chamber). A more exact calculation would depend on many details including quantity order. The cost per system can vary by as much as a factor of 2 depending on the operational parameters as varied above.

CONCLUSIONS

At 2.45 GHz, a metallic deposit was collected on a quartz plate. In nitrogen gas and the addition of sugar, a significant amount of deposit was collected. The deposit is probably Zn and when confirmed, it will prove that selective volatization of Zn (and possibly other metals) is possible with microwaves. More Zn appears to volatize when N was used. The lack of O2 may prevent the formation of ZnO which would not volatize. The addition of