



Optimizing yield of metallic zinc tapped from a zinc smelter by studying factors causing zinc losses to dross

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Synopsis

Zincor experienced significant losses of metallic zinc to dross during the melting of zinc cathode plates. In this study five factors affecting the formation of dross are identified from literature. Dross from both the plant and that produced in the laboratory is characterized using XRD. An empirical model, based on laboratory-scale investigations, was developed to quantify the effect these factors on their own or in combination with each other has on the amount of zinc loss to dross. The predictive capability of the model is evaluated based on the laboratory-scale investigations. Predictions are made on the effects that heat treating the cathode plates prior to melting, increasing the cathode plate thickness, washing and drying prior to melting, and loading the furnace in a controlled manner have on the amount of zinc loss to dross.

Keywords: Zinc, dross, optimize, smelter, yield, losses, empirical, model, XRD.

Introduction

Zincor is situated in Springs, South Africa and is a primary producer of metallic zinc and zinc-based alloys. At Zincor, metallic zinc cathode plates are produced by an electrowinning process. These plates are melted in induction furnaces and cast into ingots of various sizes, which are sold to end-users.

Zincor experienced problems with the formation of zinc dross in the furnaces. A substantial amount of the molten zinc metal from the melt was lost to the dross due to oxidation and entrapment. Zincor wanted to maximize the yield of molten zinc to cast ingots since the dross sold at a much lower price compared to metallic zinc.

Zincor therefore approached the University of Pretoria to assist in an investigation and the objectives were to characterize the zinc dross—in an attempt to quantify the amount of zinc lost to the dross as oxide or due to entrapment—and to propose methods of minimizing the loss of metallic zinc to dross through oxidation and entrapment.

Zincor process description

The process flow at Zincor has been described in detail elsewhere¹. The process stages of interest to this study were the cell house, melt

house, and the dross processing operation. These stages will now be described in more detail based on the flowsheet indicated in Figure 1.

Cell house

Purified zinc sulphate enters the cell house from a neutral leaching and purification stage. In the cell house, zinc is plated onto aluminium cathodes by electrolysis. The cathodes are stripped manually every 24 hours and replaced in order to repeat the plating process. The anodes consist of lead that contains 0.5% Ag and 0.05% Ca. The current density of the cells is approximately 600 A/m²¹. There are 40 cathodes and 41 anodes in each cell with 12 cells in each bank and 14–16 banks to complete the circuit¹.

Melt house

The cathode plates produced from the electro-winning stage are charged to several induction furnaces in the melt house². The plates are charged with ammonium chloride which fluxes any oxides formed. Three furnaces are utilized for the casting of 25 kg slabs; one furnace for the casting of one ton and two ton jumbo blocks; one furnace for the melting of an aluminium master alloy containing 20% Al; one pre-alloy furnace for the alloying of aluminium and zinc; one zinc dust furnace; and one lead melting furnace with a debasing pot².

Due to the difference in density dross tends to float on top of the molten zinc. The dross is scraped off the molten metal and cooled in air before it is sent to the dross plant for further processing². The maximum amount of zinc recovered to the ingot is in the range of 94–96 per cent which means that a minimum of 4–6 per cent of the molten zinc is lost to the dross³.

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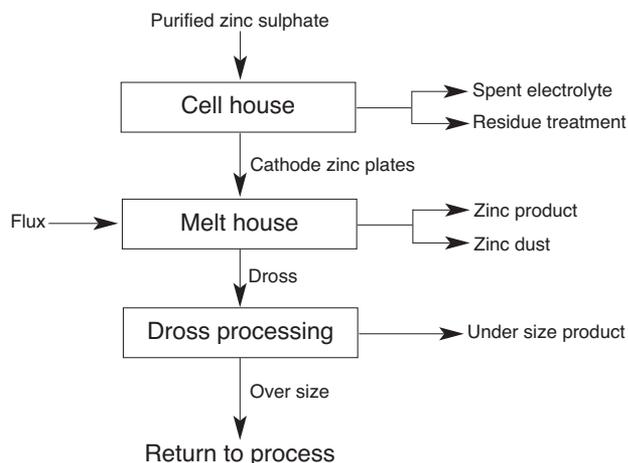


Figure 1—Electrowinning (cell house), melting (melt house) and dross processing stages of Zincor process—after Van Dyk¹ and Du Toit²

Dross processing

At the dross plant the dross is screened and milled. The oversize fraction is fed back into the process at the roasters². The milled fine fraction dross (brown ash) is sold to other dross processing plants to recover any zinc units left. The dross is sold to dross processing companies at a much lower price compared with the zinc ingot price.

Zinc dross constituents

Zinc dross consists mostly of zinc oxide due to the oxidation of zinc in the furnace². The zinc oxide film, in the form of a powder or an ash-like substance, forms on the surface of the molten zinc during melting. Other minor phases present in the dross may be chloride type phases included in the flux; zinc hydroxide phases which form due to the presence of water; zinc sulphate from misplaced zinc electrolyte reporting to the melting furnace, and metallic zinc entrapped in the dross during the scraping-off process².

Factors affecting zinc dross formation

According to the literature, several factors influence the extent to which dross forms. Each of the factors will be discussed in detail below as they lead to the hypothesis tested in this project.

Melting zinc cathode plates

The correct method of melting zinc cathode plates in a furnace is first to form a pool of molten metal by melting zinc ingots and flux³. Once a molten pool of metallic zinc and flux has formed the cathode plates are charged directly into the molten metal³. The objective is to minimize the time hot cathode plates are in contact with the air to minimize the oxidation of zinc.

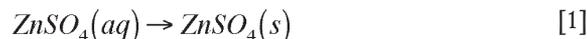
Surface area to volume ratio

When melting metallic aluminium, aluminium dross forms in a similar manner to zinc dross. Literature on the melting of metallic aluminium indicates that plate thickness plays a role in the amount of dross formed during melting. Experimental data in Figure 2 indicates that as the gauge of the plate becomes thinner, the melt loss in the furnace increases⁴. The reason is the increase in surface area to volume ratio. As the

gauge of the plate decreases, it increases the surface area per unit weight of charge exposed to the oxidizing environment in the furnace. More oxidation will occur, forming more dross^{4,5}.

Liquids present on plates during charging

If zinc electrolyte from the electrowinning process clings to the zinc cathode plates when charged to the furnace, the zinc electrolyte will report to the dross as per Reaction [1]⁶.



The zinc electrolyte contributes to the mass of the zinc dross⁵. The effect can be counteracted if the zinc plates are washed with water before charging to the furnace.

If water is present on the zinc cathode plates it could cause oxidation during stacking and during charging or melting according to Reactions [2] and [3]^{3,6} forming either zinc hydroxide ($\text{Zn}(\text{OH})_2$) or zinc oxide (ZnO).

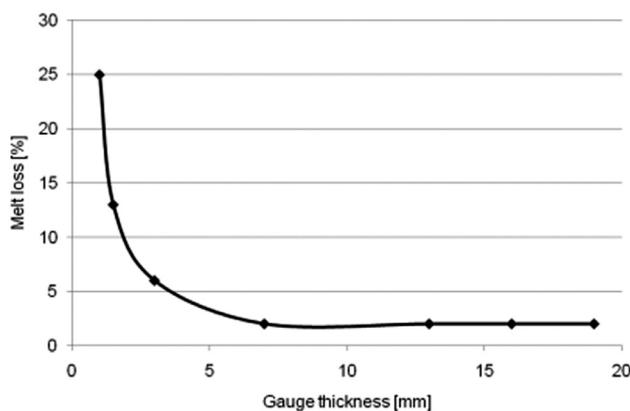


At room temperature Reaction [3] is thermodynamically more stable than Reaction [2] ($G^\circ = -64.630 \text{ kJ/mol}$ and $G^\circ = -71.5882 \text{ kJ/mol}$ respectively), whereas at 530°C , Reaction [2] is thermodynamically more stable than Reaction [3] ($G^\circ = -166.094 \text{ kJ/mol}$ and $G^\circ = -109.848 \text{ kJ/mol}$)⁷.

If the plates are washed with water but not dried $\text{Zn}(\text{OH})_2$ or most likely ZnO will form when the plates are stacked at low temperatures and ZnO when charged at high temperatures into the furnace. $\text{Zn}(\text{OH})_2$ might convert to ZnO on heating³. The ZnO that is formed will report to the dross.

To counteract these reactions, plates should be dried properly after washing and before stacking or charging them to the furnace.

Figure 2—The effect of the gauge thickness of aluminium scrap plates



charged to the furnace on melt loss—redrawn from Nilmani and Makhijani⁴

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Heat treatments

Hydrogen may be trapped in the cathode plates during electrowinning depending on the current efficiency of the electrowinning stage. During electrowinning most modern plants operate at a current efficiency of approximately 90% during good operation⁸. This means that hydrogen evolution might occur and that some of the hydrogen may be trapped in the zinc cathode plates, which can be released at a later stage during melting⁶.

If there is entrapped hydrogen present in the plates during melting and the hydrogen is released rapidly, it could cause small and easily oxidizable particles of zinc to be blown off the melt⁵. The idea of performing a heat treatment is to release the hydrogen (if any is present) from the plates before melting thus reducing dross formation⁵.

From literature, by heat treating the plates before melting, the amount of zinc lost to dross can be reduced by as much as 35 per cent depending on the heat treatment applied⁵. Knechtel and Flon⁵ claimed that heat treatment temperatures between 275°C–370°C with times ranging from 10–60 minutes were suitable and that an ideal condition would be at 290°C for 30 minutes⁵. It is important that heat treatment is done under a protective atmosphere to limit the amount of oxidation of the zinc.

Charging technique

At the time of the investigation, a choke-feeding system was used to charge the plates into the furnace. Charging in such a manner causes turbulence on the surface of the melt¹ thus breaking the barrier between the flux and the molten zinc and exposing the molten zinc to the oxidizing atmosphere inside the furnace. The choke-feeding system does not only cause oxidation of the molten zinc, but it also causes destruction of the furnace lining which will report to the dross⁹. Using a grab-feeding system and charging the cathode plates in a controlled manner into the furnace will minimize turbulence and therefore oxidation of liquid zinc and damage to refractories.

Hypothesis statement

Based on the factors influencing the extent to which dross forms reported by literature, the following hypothesis was stated:

By managing the following factors, the amount of metallic zinc lost to dross in a melting furnace will be minimized:

- Plate thickness
- Heat treatment
- Water
- Electrolyte and
- Turbulence.

Experimental procedure

Sample preparation

Zincor supplied a zinc dross sample, two 24 hour electrowon cathode plates and one 30 hour electrowon cathode plate. The cathode plates were prepared on the plant by rinsing them immediately with water after stripping followed by drying. At the laboratory the cathode plates were cut into 35 mm × 35 mm squares using a guillotine. The sample size was

determined by the diameter of the laboratory scale resistance furnace crucible of 65 mm.

Design of experiments

A statistical approach was taken to design the experiments for the project¹⁰. As there were five factors of interest (plate thickness, heat treatment, water, electrolyte and turbulence) with two levels (high and low) each the full 2^k factorial design method was selected. The method required 32 experiments to test the effect different factors individually have on the formation of zinc dross as well as their interactions with one another, and incorporates repeatability to some extent.

The specific factors chosen and their levels were:

- Heat treatment at 290° for 30 minutes (the high value was with heat treatment [+1] and the low value without heat treatment [-1])
- Thickness of plate (the high value was a 30 hours electrowon plate [+1] and the low value a 24 hours electrowon plate [-1])
- Water present (the high value was a wet sample [+1] and the low value a dry sample [-1])
- Electrolyte present (the high value was a wet sample [+1] and the low value a dry sample [-1]) and
- Turbulence (the high value with stirring [+1] and the low value without stirring [-1]).

The response measured was the amount of zinc lost (%) and the factors kept constant were time to melt (30 min) and amount of NH_4Cl flux added (1 kg/ton of cathode).

To design the combinations in which the 32 experiments had to be executed an add-in to Microsoft Excel was used. The 32 experiments were randomized and the design matrix is displayed in Table I.

Execution of experiments

Each of the 32 experiments involved a melting step which was executed in a resistance heating furnace. The furnace temperature was controlled by an automated controller at a set-point of 530°C.

The dry cathode plate samples, 1 kg NH_4Cl flux per ton of cathode plate charged and the iron-based crucible were weighed separately before placing them into the furnace.

The samples were held at 530°C for 30 minutes to ensure that the cathode plates melted². After 30 minutes the crucible with the molten zinc and dross was removed from the furnace. The dross on the molten metal surface was scraped off with a stainless steel spoon into a metal bowl. The molten metal remained in the iron-based crucible where it solidified.

When cooled the iron-based crucible with metallic zinc was weighed and the weight recorded. The scraped off dross was screened at 2360 μm and the oversize and undersize fractions weighed and recorded. A mass balance was performed around the circuit to determine the amount of zinc lost to dross.

When experiments with water and electrolyte were performed the plates were fully immersed in water or electrolyte before charging them to the furnace. For the experiments involving turbulence, the melt was stirred. For the heat treatments, the samples were heat treated in a muffle furnace for 30 minutes at 290°C prior to charging into the resistance furnace.

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Table I

Design matrix for experiments

Exp #	HT	Thick	W	E	T	Exp #	HT	Thick	W	E	T
1	1	-1	-1	1	-1	17	1	-1	-1	-1	-1
2	-1	-1	-1	-1	-1	18	1	1	1	-1	1
3	-1	1	-1	-1	1	19	1	1	1	-1	-1
4	-1	1	1	1	-1	20	1	1	-1	-1	-1
5	-1	1	1	-1	-1	21	-1	-1	-1	-1	1
6	-1	-1	1	-1	-1	22	-1	-1	1	-1	1
7	1	-1	1	1	1	23	1	-1	1	-1	1
8	1	1	-1	1	-1	24	1	-1	1	1	-1
9	-1	1	-1	1	1	25	1	-1	1	-1	-1
10	1	-1	-1	1	1	26	-1	-1	1	1	1
11	-1	1	-1	-1	-1	27	-1	1	1	-1	1
12	1	1	-1	-1	1	28	1	1	1	1	-1
13	1	-1	-1	-1	1	29	-1	-1	-1	1	1
14	1	1	1	1	1	30	-1	1	-1	1	-1
15	-1	-1	-1	1	-1	31	1	1	-1	1	1
16	-1	1	1	1	1	32	-1	-1	1	1	-1

HT: heat treatment at 290° for 30 minutes (1 = with; -1 = without); Thick : cathode plate thickness (1 = 30 hour electrowon; -1 = 24 hour electrowon); W: water (1 = with; -1 = without); E: electrolyte (1 = with; -1 = without) and T: turbulence (1 = with; -1 = without)

Table II

Normalized semi-quantitative mineral composition in mass per cent of dross received from the Zincor plant and produced in the University of Pretoria laboratory

Component	Plant	Laboratory
ZnO (zincite)	61	62
Zn (metallic zinc)	13	27
Other	26	11

Both the as-received zinc dross from the plant and the zinc dross produced in the laboratory were characterized using semi-quantitative X-ray diffraction (XRD).

Results and discussion

Characterizing the zinc dross

Table II contains the semi-quantitative XRD results of the zinc dross sampled at the plant and the zinc dross sampled in the laboratory. Both samples consisted primarily of ZnO containing in excess of 60 per cent by mass. Both samples contained significant amounts of metallic zinc but the dross prepared in the laboratory contained twice the amount of metallic zinc contained in the dross sampled at the plant. The dross sampled at the plant contained twice the amount of other species contained in the dross sampled in the laboratory. The other species in the dross sampled at the plant consisted of zinc-based hydroxides and zinc-based sulphates which could be attributed to the presence of water and the presence of electrolyte on the cathode plates. The other species in the dross sampled at the laboratory consisted of zinc sulphide, sodium fluoride and magnetite. The former two were attributed to the flux and the latter to oxidation of the iron-based crucible.

Quantifying the effect of the factors on zinc dross formation

When all responses (per cent zinc lost) were added to the design matrix the results were analysed with DOE. All factors (individual and interactions) were selected to evaluate for the best fit model at a 95 per cent confidence level. After 9 948 runs, the models with a maximum of 6 terms were evaluated and the model with the highest value of the coefficient of determination ($R^2 = 0.821$) was selected as indicated in Equation [4].

$$\begin{aligned} \% \text{ zinc lost} = & 2.789 - 0.416^* A - \\ & 0.404^* B + 0.172^* C + 0.233^* A^* B + \\ & 0.297^* D - 0.302^* D^* E \end{aligned} \quad [4]$$

where:

- A: heat treatment at 290° for 30 minutes
- B: thickness of plate
- C: water present
- D: electrolyte present
- E: turbulence present

From Equation [4] it can be seen that all individual factors had a significant effect on the mass per cent zinc lost to dross. Having turbulence and electrolyte present in combination and heat treatment and thickness in combination had an additional effect on the mass per cent zinc lost to dross.

Analysis of residuals and model checking

In any designed experiment it is important to evaluate the predictive capability of the model. Factors that were investigated included¹¹:

- Coefficient of determination (R^2) where a value close to 1.0 indicates a good fit of the data and therefore a model with acceptable predictive capability
- Residuals, i.e. the difference between the observed values and the predicted values where small values scattered around zero is indicative of a model with acceptable predictive capability and

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- ▶ Studentized residuals where 95 per cent of the studentized residuals falling within the range [-2, 2] is indicative of a model with acceptable predictive capability.

As already mentioned the R^2 of the model in Equation [4] was 0.821—refer to Figure 3—which indicated that the model could account for 82.1 per cent of the variability in the data which was acceptable. The residuals in Figure 4, where small values scattered around zero, and studentized residuals in Figure 5, where 100 per cent of the studentized residuals fell within the range [-2, 2], indicated that the model in Equation [4] had acceptable predictive capability.

Significance of the model

Contour diagrams were constructed in order to quantify the effect that combinations of the factors had on the predicted amount of zinc loss to dross. Some of the results are summarized below:

- ▶ When melting a cathode plate electro-won for 30 hours and heat treated at 290° for 30 minutes, the zinc loss to dross could be reduced to 1.4–1.6 per cent
- ▶ When melting a cathode plate electro-won for 24 hours and not heat treating, the zinc loss to dross could be 3–3.2 per cent zinc
- ▶ When melting a cathode plate covered with both water and electrolyte, the zinc loss to dross could be 4.5–5.8 per cent zinc
- ▶ When melting a cathode plate with no water or electrolyte present, the zinc loss to dross could be 3–3.3 per cent zinc
- ▶ When charging a cathode plate electro-won for 30 hours in a controlled manner and not causing any turbulence, the zinc loss to dross could be 1.8–2.1 per cent zinc and
- ▶ When charging a cathode plate electro-won for 24 hours in an uncontrolled manner and causing turbulence, the zinc loss to dross could be 3.6–3.9 per cent zinc.

Conclusions

Zinc dross consisted primarily of ZnO (>60 per cent by mass) with significant amounts of entrained zinc metal (~30 per cent by mass) and flux (~10 per cent by mass) present in dross produced in a laboratory and significant amounts of

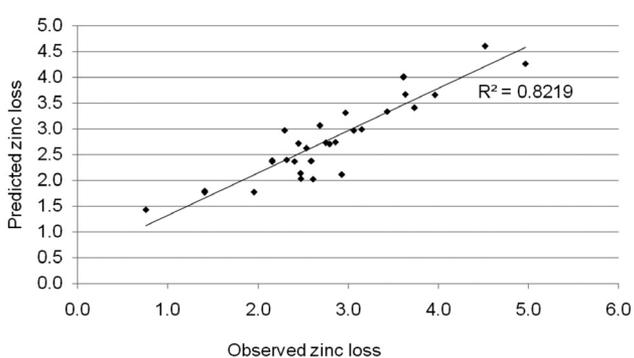


Figure 3—Relationship between the results observed in the laboratory and the predicted results from the model

entrained metal (10 per cent by mass) and zinc-based hydroxides and sulphates present (~30 per cent by mass) in dross produced in the plant.

An empirical model with high predictive capability and an acceptable account of the variability in the data produced in the laboratory scale furnace was developed. The model indicated that all five factors investigated: heat treating the electrode plate prior to melting at 290° for 30 minutes; increasing the thickness of the electrode plate by increasing the plating time; ensuring that the electrode plate is washed and dried before charging; and charging the furnace in a controlled manner individually had a significant influence on minimizing the amount of zinc loss to dross while the combination of having both electrolyte present and charging the furnace in an uncontrolled manner further increased the amount of zinc loss to dross.

It could therefore be concluded that the hypothesis stated was true.

As the model quantified the predicted amount of zinc lost to dross, the financial impact of not managing the factors investigated could therefore be quantified.

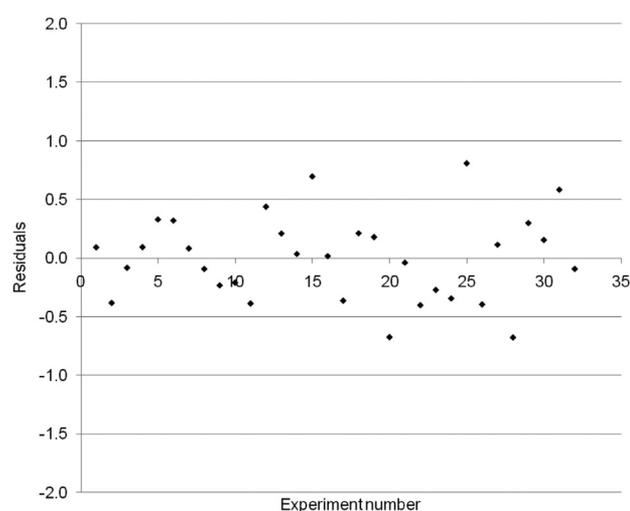


Figure 4—Residuals of all 32 experiments

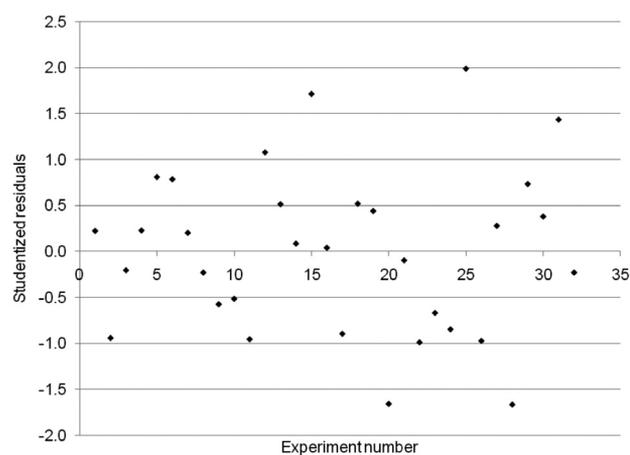


Figure 5—Studentized residuals of all 32 experiments

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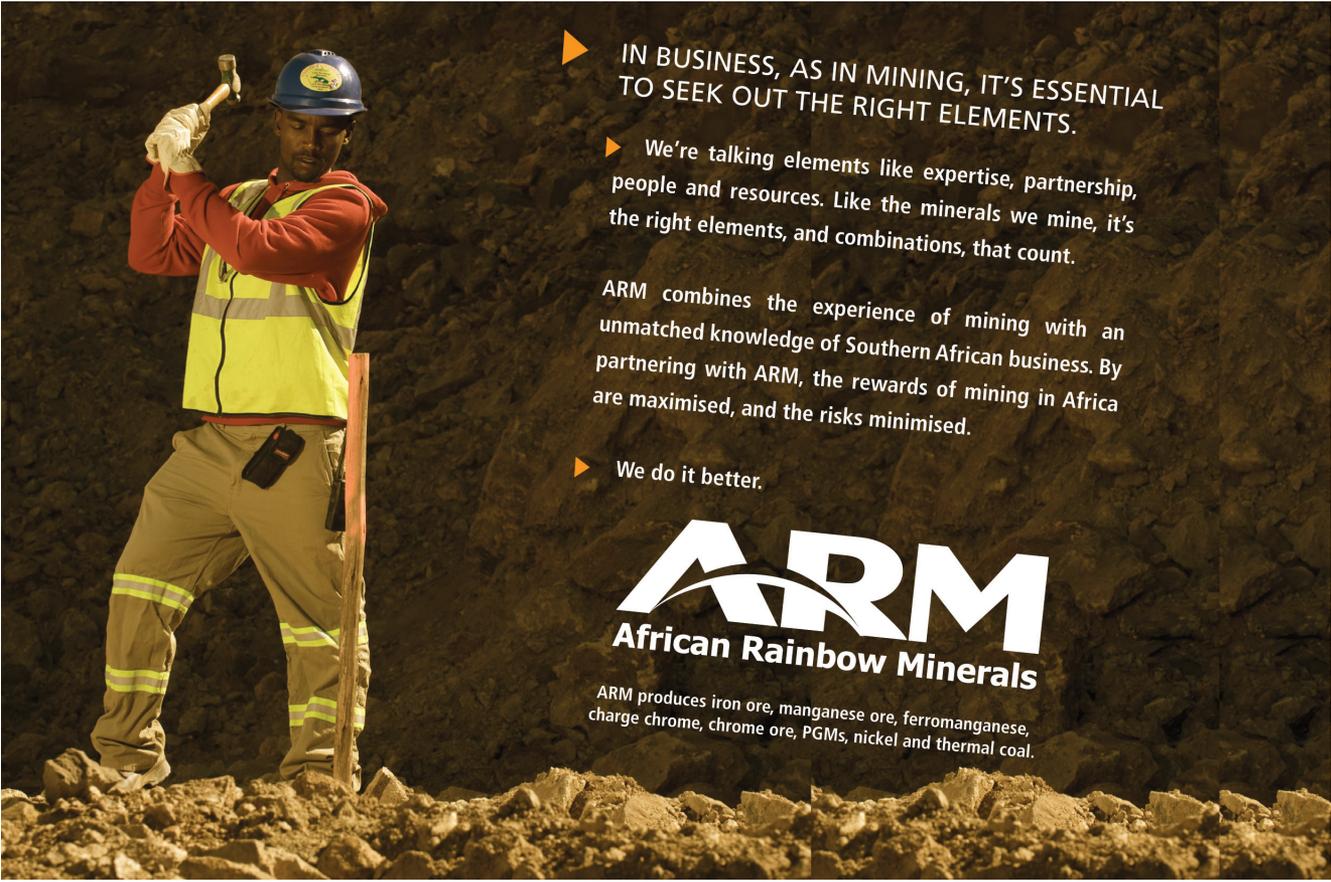
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