

## AL07 - Measurement of Metal Inventory in Pots with Zinc Dilution

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### Abstract

Copper dilution process is practiced worldwide in the field of aluminium electrolysis. In this process, copper is added to the aluminium metal to establish the metal inventory in the pot by analyzing the % increment of copper in molten metal. By adding a certain amount of copper and analyzing copper content in aluminium before and after copper is added, it is possible to calculate the metal reservoir. Copper is chosen because it is neutral to bath chemistry when inserted in the liquid bath. This paper is about the use of zinc dilution instead of copper dilution for checking the metal inventory in the pot. Zinc has many advantages over copper due to its low heat of fusion, low melting point and its diamagnetic nature which is one of the most important parameters while considering any material in a high amperage potline. Zinc is also available in the market at one fourth of the price of copper. This paper uses Ellingham diagram, EMF series, Gibbs free energy for establishing the fact that zinc is a thermodynamically stable element, and that it will have no impact on bath chemistry and can be used as an alternative to copper dilution for checking the metal inventory in the pot. Many tests in the pots have shown that that the zinc dilution method is accurate, consistent and reliable.

**Keywords:** Aluminium pot metal inventory measurement, zinc dilution in liquid aluminium, Ellingham diagram, EMF series, heat of fusion.

### 1. Introduction

Copper dilution is used in the aluminium industry for checking the metal inventory in the pot. One of the major reasons for choosing copper is that it does not have an impact on bath chemistry and the purity of final finished product such as ingot, wire rod etc. obtained from cast house. Also, according to emf series a more reactive element replaces a less reactive element from its solution and as shown in Figure 1, aluminium which is more reactive element is placed above copper which is less reactive element so copper is neutral to bath chemistry.

Zinc shows the same behavior as copper as position of zinc in the emf series (as shown in Figure 1) is placed below aluminium, so it is also neutral to bath chemistry and also zinc does not affect the purity of final finished product obtained from cast house due to very low content of zinc in metal after the process of zinc dilution. While considering zinc for dilution process a number of factors are taken into account including comparison of properties of zinc and copper such as heat of fusion, magnetic properties, melting point and density in liquid phase as shown in Table 1.

As shown in Table 1 low melting point of zinc along with low heat of fusion, helps in faster dilution of zinc as compared to copper and also the diamagnetic nature of zinc is very important in a high amperage potline.

**Table 1. Comparison of copper and zinc properties.**

Properties	Copper	Zinc
Melting point	1083 °C	420 °C
Heat of fusion (kJ/mol)	13.2	7.32
Magnetic ordering	Diamagnetic	Diamagnetic
Density in Liquid phase(kg/m <sup>3</sup> )	8020	6570

Equilibrium (Oxidants ↔ Reductants)	E° (volts)
Lithium: Li <sup>+</sup> (aq) + e <sup>-</sup> ↔ Li(s)	-3.03
Potassium: K <sup>+</sup> (aq) + e <sup>-</sup> ↔ K(s)	-2.92
Calcium: Ca <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Ca(s)	-2.87
Sodium: Na <sup>+</sup> (aq) + e <sup>-</sup> ↔ Na(s)	-2.71
Magnesium: Mg <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Mg(s)	-2.37
Aluminum: Al <sup>3+</sup> (aq) + 3e <sup>-</sup> ↔ Al(s)	-1.66
Zinc: Zn <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Zn(s)	-0.76
Iron: Fe <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Fe(s)	-0.44
Lead: Pb <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Pb(s)	-0.13
Hydrogen: 2H <sup>+</sup> (aq) + 2e <sup>-</sup> ↔ H <sub>2</sub> (g)	0.00
Copper: Cu <sup>2+</sup> (aq) + 2e <sup>-</sup> ↔ Cu(s)	+0.34
Silver: A <sup>+</sup> (aq) + e <sup>-</sup> ↔ Ag(s)	+0.80
Gold: Au <sup>3+</sup> (aq) + 3e <sup>-</sup> ↔ Au(s)	+1.50

**Figure 1. Electrochemical series of metals [1].**

According to Ellingham diagram (plot of Gibbs free energy vs Temperature) shown in Figure 2, the change in Gibbs free energy of formation of aluminium oxide at (950-1000 °C) is more negative as compared to Gibbs free energy of formation of zinc oxide so aluminium oxide is more stable as more negative value of ΔG means the more stability of formation of oxide.

## 2. Experimental Procedure

To check the practical feasibility of zinc dilution in pots for calculation of metal inventory various tests are performed on 15-20 pots covering all cathode types like 100 % graphitic, 50 % graphitic and 30 % graphitic cathodes. Both zinc and copper plates are inserted simultaneously in the same pot, i.e., 2 kg each of zinc and copper plates from tap end and 2 kg each of zinc and copper plates from duct end. Purity of both zinc and copper plates is measured in central laboratory, Jharsuguda and metal/bath height (ML1) is measured at both the tap end and duct end before insertion of zinc and copper plates in the pot as shown in Figure 3. Metal sample is taken from both tap end (T<sub>0</sub>) and duct end (D<sub>0</sub>) before the insertion of copper and zinc plates. Voltage and line current were also recorded before starting the dilution test. After insertion of preheated zinc and copper plates metal sample is taken out from the pot 1-hour interval each up to 4 hours and poured into the mould as shown in Figures 4 and 5. The samples were numbered as T<sub>1</sub>, D<sub>1</sub>, T<sub>2</sub>, D<sub>2</sub>, T<sub>3</sub>, D<sub>3</sub>, T<sub>4</sub>, D<sub>4</sub>.

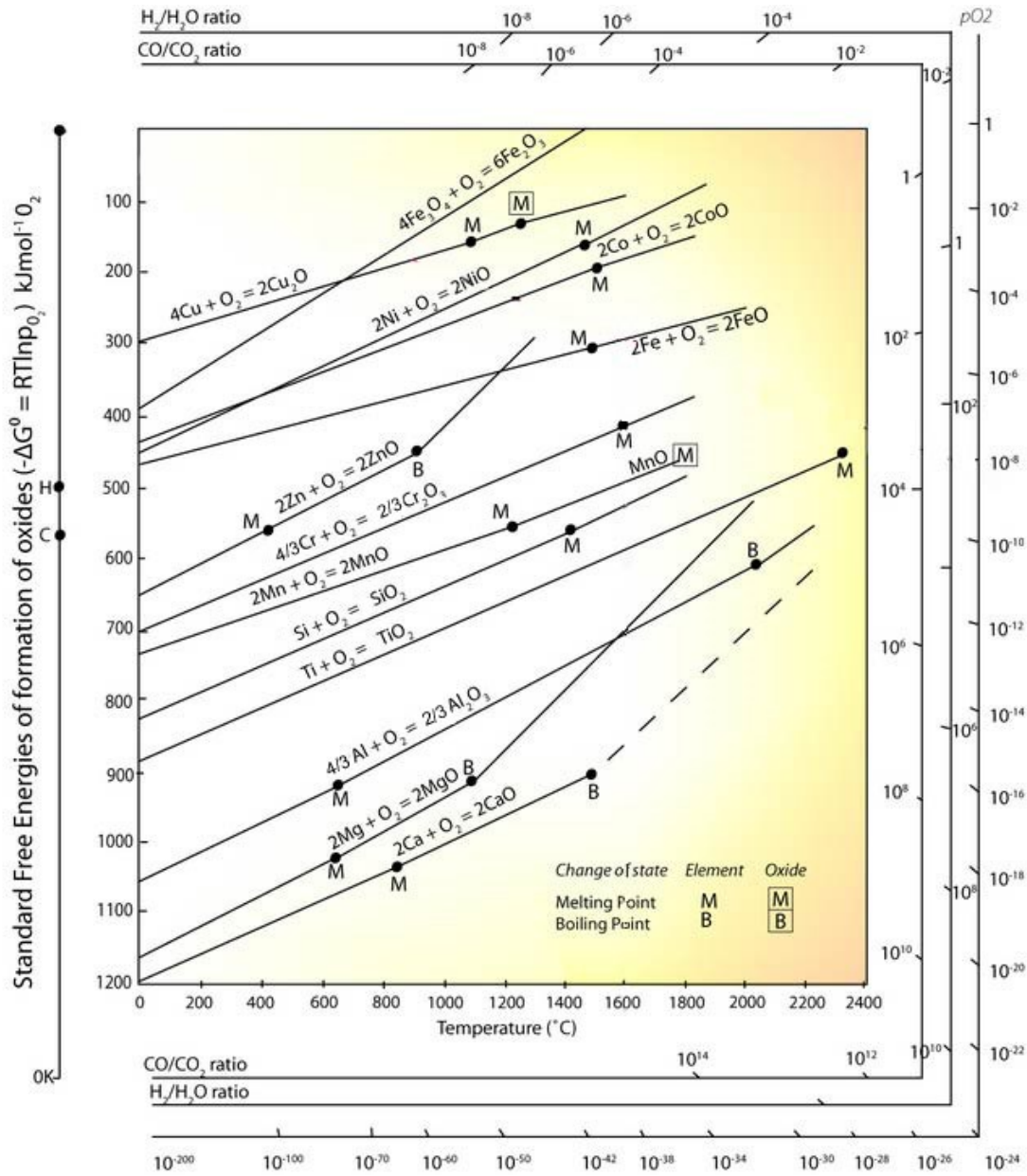


Figure 2. Ellingham diagram [2].



Figure 3. Metal/bath height measurement.



Figure 4. Taking metal sample.

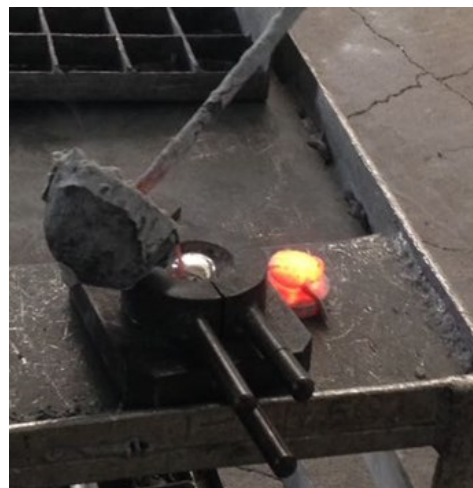


Figure 5. Metal pouring in mould.

Metal/bath height is remeasured (ML2) from both tap end and duct end after taking all the metal samples. As there is zinc content in the raw materials such as anode and alumina, the variation of zinc content in anode and in alumina is monitored continuously over the duration of the test. Zinc and copper content in the metal is measured from the sampling data before the start of dilution process and after the completion of dilution process; increment in zinc and copper percentage in the metal is noted. Metal sample analysis is done in the central lab, Jharsuguda using optical emission spectrophotometer (OES).

### 3. Calculation of Background Zinc in the Metal

The possible sources of zinc inside the pot are zinc coming from baked anodes and from alumina. Average ZnO content in primary alumina in the period from April to September 2020 was 9 ppm with minimum of 7 ppm and maximum of 12 ppm. The content of zinc in baked anodes in the period from April to September 2020 was 38 ppm with minimum of 25 ppm and maximum of 52 ppm. Average background content of zinc in the metal was 20 ppm; these are last one-year data obtained from Central Lab, Jharsuguda (ISO 9001:2015, ISO 14001:2015 and OHSAS18001:2007 Certified). Calculations are done to estimate the contribution of zinc in the pot from baked anode and alumina during the four hours of dilution process as shown in Tables 2 and 3, respectively.

**Table 2. Theoretical calculation for Zn contribution by baked anodes during 4 hours of Zn dilution.**

Zinc in anodes	0.0038	%
Anode weight	1000	kg
Butt weight	250	kg
One anode consumption in 28 days	750	kg
One anode consumption per day	26.786	kg
One anode consumption in 4 hours	4.46	kg
Zn entering bath per anode	0.000170	kg
Zn entering bath for 40 anodes	0.0068	kg
Baked anode contribution of Zn in metal in 4 hours	6.8	g
Baked Anode Contribution of Zn in metal in 4 hours (6.7 g in 429.0 kg of Al produced in 4 h)	16	ppm

**Table 3. Theoretical calculation for Zn contribution by alumina for 4 hours of Zn dilution.**

ZnO in alumina	0.00094	%
Zn from alumina (80.34 % of ZnO)	0.00076	%
Total alumina feeding frequency in 4 h	192	
Alumina dosage per feeding	4.5	kg
Total alumina feeding in 4 h	825	kg
Zn contribution in metal from alumina in 4 h	0.0063	kg
Zn contribution in metal from alumina in 4 h (6.6 g in 429.0 kg of Al produced in 4 h)	15	ppm

By these calculations, total Zn content in the metal from anodes and alumina is 31 ppm, but only 20 ppm is actually found in the metal by laboratory measurements. The reason for this discrepancy has not been investigated. In the tests, the measured values of background Zn in the metal were used.

The metal inventory is calculated in various pots with different cathode types, using copper and zinc dilution method and excellent results have been found most of the time.

### 3.1. Metal Inventory Calculations by Zinc and Copper Dilution

After taking various measurements such as metal/bath height, metal sampling before the start of dilution process and after the completion of dilution process metal inventory in various pots was calculated. Metal inventories for a pot with 30 % graphitic cathode are calculated in detail in Tables 4-5 and for 100 % graphitic cathode in in Tables 6-7. All the metal inventory calculations were verified in central lab of Vedanta, Jharsuguda and all the metal inventory calculations were made according to Standard Operating Procedure (SOP) of copper dilution test of Vedanta Aluminium Limited, Jharsuguda (ISO 9001:2015, ISO 14001:2015, OHSAS18001:2007). The tests were carried out at 340 kA. During these tests, no anode effect occurred and the pots were in normal conditions. The metal inventory was calculated by the following equations:

$$\text{Metal reserve in the pot } (t) = \frac{\text{Pure Cu or Zn addition (kg)} \times 100}{\text{Cu or Zn increment in metal (\%)} \times 1000} - \text{Metal production in 4 hours } (t)$$

$$\text{Metal production in 4 hours } (t) = 8.054 \times kA \times \frac{CE(\%)}{100} \times \frac{4}{24} \times \frac{1}{1000}$$

**Table 4. Metal inventory by copper dilution in 30 % graphitic pot.**

<b>Cu Dilution</b>			
<b>Date</b>			<b>21-May</b>
<b>Pot number</b>			<b>48XX</b>
<b>Before Dilution</b>	Tap end	<b>Unit</b>	
<b>Metal height</b>		cm	29
<b>Bath height</b>		cm	16
<b>Bath temperature</b>		°C	958
<b>Voltage</b>		V	4.18
<b>Copper added at</b>	Tap end	kg	2.002
<b>Copper added at</b>	Duct end	kg	2.002
<b>Copper added total</b>	.	kg	4.004
<b>Cu in metal before copper addition</b>	Tap end	%	0.0001
	Duct end	%	0.0001
	Average	%	0.0001
<b>Cu in metal after the completion of copper dilution test</b>	Tap end	%	0.0109
	Duct end	%	0.0109
	Average	%	0.0109
<b>Increment in Cu in metal</b>		%	0.0108
<b>Copper added</b>		kg	4.004
<b>Copper purity (%Cu)</b>		%	99.3
<b>Pure copper addition</b>		kg	3.9760
<b>Metal reserve in the pot</b>	End test	t	36.815
<b>Current efficiency (CE)</b>	Average	%	94.00
<b>Current</b>		kA	340.00
<b>Metal production in 4 h</b>		t	0.429
<b>Metal reserve in the pot</b>	Start test	t	36.386
<b>Metal per 1 cm height</b>		t	1.213

**Table 5. Metal inventory by zinc dilution in 30 % graphitic pot.**

<b>Zn Dilution</b>			
<b>Date</b>			<b>21-May</b>
<b>Pot number</b>			<b>48XX</b>
<b>Before Dilution</b>	Tap end	<b>Unit</b>	
<b>Metal height</b>		cm	29
<b>Bath height</b>		cm	16
<b>Bath temperature</b>		°C	958
<b>Voltage</b>		V	4.18
<b>Zinc added at</b>	Tap end	kg	1.800
<b>Zinc added at</b>	Duct end	kg	1.600
<b>Zinc added total</b>	.	kg	3.400
<b>Zn in metal before zinc addition (measured)</b>	Tap end	%	0.0015
	Duct end	%	0.0015
	Average	%	0.0015
<b>Zn in metal after the completion of zinc dilution test</b>	Tap end	%	0.0109
	Duct end	%	0.0107
	Average	%	0.0108
<b>Increment in Zn in metal</b>		%	0.0093
<b>Zinc added</b>		kg	3.400
<b>Zinc purity (%Zn)</b>		%	99.99
<b>Pure zinc addition</b>		kg	3.3997
<b>Metal reserve in the pot</b>	<b>End test</b>	<b>t</b>	<b>36.555</b>
<b>Current efficiency</b>	Average	%	94.00
<b>Current</b>		kA	340.00
<b>Metal production in 4 h</b>		t	0.429
<b>Metal reserve in the pot</b>	Start test	t	36.127
<b>Metal per 1 cm height</b>		t	1.204

It can be observed from the metal inventory calculations in Tables 4 and 5 that the metal inventory by copper dilution in pot 48XX with 30 % graphitic cathode is 36.386 tonnes and metal inventory by zinc dilution is 36.127 tonnes. This is good agreement between these two methods.

**Table 6. Metal inventory by Cu dilution in 100 % graphitic pot.**

<b>Cu Dilution</b>			
<b>Date</b>			<b>19-Jun</b>
<b>Pot number</b>			<b>46XX</b>
<b>Before Dilution</b>	Tap end	<b>Unit</b>	
<b>Metal height</b>		cm	28
<b>Bath height</b>		cm	17
<b>Bath temperature</b>		°C	959
<b>Voltage</b>		V	4.18
<b>Copper added at</b>	Tap end	kg	2.018
<b>Copper added at</b>	Duct end	kg	2.008
<b>Copper added total</b>	.	kg	4.026
<b>Cu in metal before copper addition</b>	Tap end	%	0.0018
	Duct end	%	0.0017
	Average	%	0.00175
<b>Cu in metal after the completion of copper dilution test</b>	Tap end	%	0.0120
	Duct end	%	0.0122
	Average	%	0.0121
<b>Increment in Cu in metal</b>		%	0.01035
<b>Copper added</b>		kg	4.026
<b>Copper purity (%Cu)</b>		%	99.3
<b>Pure copper addition</b>		kg	3.9990
<b>Metal reserve in the pot</b>	End test	t	38.638
<b>Current efficiency</b>	Average	%	94.00
<b>Current</b>		kA	340.00
<b>Metal production in 4 h</b>		t	0.429
<b>Metal reserve in the pot</b>	Start test	t	38.209
<b>Metal per 1 cm height</b>		t	1.365

**Table 7. Metal inventory by zinc dilution in 100 % graphitic pot.**

<b>Zn Dilution</b>			
<b>Date</b>			<b>19-Jun</b>
<b>Pot number</b>			<b>46XX</b>
<b>Before Dilution</b>	Tap end	<b>Unit</b>	
<b>Metal height</b>		cm	28
<b>Bath height</b>		cm	17
<b>Bath temperature</b>		°C	959
<b>Voltage</b>		V	4.18
<b>Zinc added at</b>	Tap end	kg	2.013
<b>Zinc added at</b>	Duct end	kg	2.005
<b>Zinc added total</b>	.	kg	4.018
<b>Zn in metal before zinc addition (measured)</b>	Tap end	%	0.0019
	Duct end	%	0.0018
	Average	%	0.00185
<b>Zn in metal after the completion of zinc dilution test</b>	Tap end	%	0.0122
	Duct end	%	0.0123
	Average	%	0.01225
<b>Increment in Zn in metal</b>		%	0.0104
<b>Zinc added</b>		kg	4.018
<b>Zinc purity (%Zn)</b>		%	99.99
<b>Pure zinc addition</b>		kg	4.0176
<b>Metal reserve in the pot</b>	End test	t	38.817
<b>Current efficiency</b>	Average	%	94.00
<b>Current</b>		kA	340.00
<b>Metal production in 4 h</b>		t	0.429
<b>Metal reserve in the pot</b>	Start test	t	38.388
<b>Metal per 1 cm height</b>		t	1.371

It can be observed from the metal inventory calculations in Table 6 and 7 that the metal inventory by copper dilution in pot no 46XX having 100 % graphitized cathode is 38.209 tonnes and metal inventory by zinc dilution is 38.388 tonnes. This is very good agreement again.

Metal inventory of various pot was calculated using the same format as in Tables 4-7. Each time, the measured background content of Cu and Zn was taken into account. Excellent results were found most of the time.

#### 4. Results and Discussion

Using the format and the calculations in Tables 4-7, metal inventory was calculated in various pots as shown in Figure 6. It can be seen from Figure 6 that calculation of metal inventory by zinc dilution gives reliable results for various pots with different cathode types. The comparative study of zinc and copper dilution indicates that the deviation in metal inventory by using zinc dilution is small and when the contributions of zinc from anodes and alumina are taken into account, the calculation of metal inventory by zinc dilution gives excellent results.

As shown in Table 8 average final zinc content in metal after dilution process is less than 150 ppm most of the times which is the zinc contribution from single pot and the ladle in which metal is sent to cast house contains metal of three different pots. So final zinc content in metal ladle sent to cast house is always balanced and within the permissible limit. Hence, dilution of zinc does not have any impact on the bath chemistry of the pot, the purity of metal and the quality of finished product such as wire rod ingot, etc.

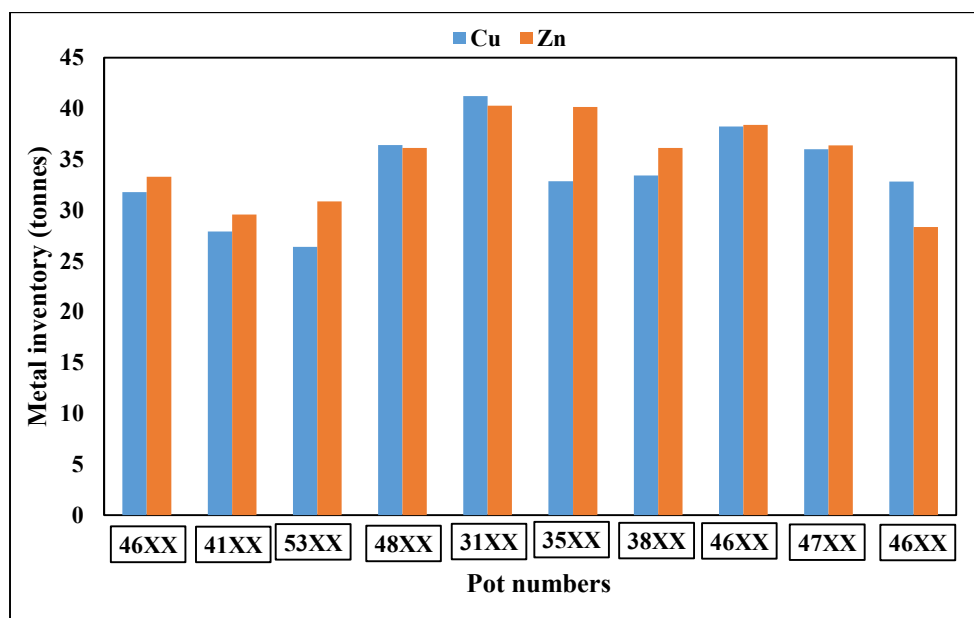


Figure 6. Comparative study of Zinc and Copper dilution test in various pots having different cathode types.

Table 8. Average final zinc content in metal after dilution process.

Pot No.	Initial Zn %	Final Zn%	Zinc weight (kg)
4602	0.0022	0.0122	4.028
4139	0.0017	0.0133	4.378
5341	0.0022	0.0125	4.148
4807	0.0015	0.0108	3.4
3109	0.0017	0.0116	4.03
3508	0.0018	0.0117	4.037
3805	0.0017	0.0115	4.888
4615	0.0019	0.0122	4.018
4735	0.0018	0.0148	4.849
3634	0.0022	0.0127	3.868
3816	0.0024	0.0117	4.067
<b>Average</b>	<b>0.0019</b>	<b>0.0124</b>	<b>4.1555</b>

## 5. Conclusions

The comparative study of metal inventory of zinc and copper dilution shows that zinc dilution can also be used for metal inventory estimation. Zinc being cheaper than copper, as price of zinc is one-fourth that of copper in the market, also gives business value. Zinc does not have an impact on the overall chemistry of the pot and it does not affect the purity of finished product be it wire rod, ingot or any primary foundry alloy as the zinc content in the ladle sent to cast house is always in the permissible range. Zinc also does not affect the properties like hardness, tensile strength of

finished cast house product, which has been verified by the technician during the production of finished goods.

Overall, results of calculation of metal inventory by zinc dilution are reliable and zinc can be considered as an option for calculation of metal inventory as well as copper.

## 6. Acknowledgement

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