

# Effect and control of impurities in electrolytic zinc production

J. D. ADHIA

THE commercial application of hydrometallurgy and electrolytic zinc production has been of recent development when compared to its strong competitor, namely, pyrometallurgy and zinc distillation. The zinc produced by pyrometallurgical methods has its own disadvantages due to (i) large losses of metal and valuable impurities, (ii) fume handling problems, (iii) limitations to equipment size, (iv) heavy repair and maintenance charges, (v) high labour costs and (vi) low quality of zinc (Table I).

TABLE I Comparison of zinc from distillation and electrolytic plants

Sl. no.	Process of zinc production	Quality of zinc metal %				
		Pb	Cu	Cd	Fe	Zn
1.	Horizontal retort distillation	0.98	0.0005	0.19	0.006	98.8
2.	Vertical retort distillation	0.13	0.0005	0.04	0.008	99.8
3.	Electrolytic	0.007	0.002	0.0004	0.0005	99.99

Electrolytic zinc production had achieved only slight success where conditions were very favourable. The high power costs, finding out a suitable insoluble and inert anode, the deposition of smooth layer of zinc in a suitable cathode-material, the preparation of a pure zinc sulphate solution and finally lack of market demand for such a pure metal were all problems in the past.

Now the situation has changed. Market demands have changed. There is demand for high, special and super-grade zinc metal from various industries. Besides, vast quantities of low grade complex zinc ores are available but are not amenable to pyrometallurgical

## SYNOPSIS

*The detrimental impurities, their effects and removal or control at different stages of the electrolytic zinc process are described in this paper.*

techniques of zinc production. The same lean ores can profitably be treated by hydrometallurgical techniques coupled with electrowinning of the metal. Besides, this process gives valuable bye-products, namely cadmium metal which is finding increasing uses in modern industries.

Zinc as metal is used for many purposes. The major use is in galvanising. The second most important use is in die-casting. It also finds use in photo-engraving and printing plates; other important uses are in the manufacture of brass and bronze alloys and in the production of quality zinc salts.

Zinc is marketed in several grades ranging from Prime Western, the lowest, to special high grade, the highest, with a purity of 99.99%. Electrolytic zinc holds its position in the market by its high purity alone (Tables II, III, IV and V).

## The process of zinc extraction

The extraction of zinc by electrodeposition usually consists of the following steps: (i) mining, (ii) concentration by flotation, (iii) roasting of the zinc blende, (iv) leaching and washing of the calcine, (v) purifying of the pregnant leach liquid from deleterious impurities in two or more stages depending on (a) the type and quantity of impurities and (b) the type of raw material used (in the case of zinc oxide, obtained from treatment of zinc residues by fuming etc., the purification steps sometimes go up to 5 stages), (vi) electrolysis of the purified feed solution and (vii) melting and casting of the cathode into zinc ingots.

All the electrolytic zinc plants follow the same general procedure; it differs from plant to plant in minor details depending on the nature of the raw material and the impurities therein.

Almost all plants use zinc blende (Table VI) as the

Mr J. D. Adhia, Managing Director, Hindustan Zinc Limited, Udaipur.

TABLE II British standards for zinc : Chemical requirements

Sl. no.	British Standard	Pb max. %	Fe max. %	Cd max. %	As and Sb max. %	Al max. %	Sn max. %	Zn min. %
1.	BS. 220 — 1947 fine zinc							
	Grade A	... 0.03	0.01	0.02	Nil	Nil	Nil	99.95
	Grade B	... 0.08	0.01	0.03	Nil	Nil	Nil	99.90
2.	BS. 221 — 1947 special zinc	... 0.20	0.05	0.25	0.02	Nil	Nil	99.5
3.	BS. 222 — 1947 foundry zinc	... 1.25	0.07	0.25	0.02	Nil	0.02	98.5
4.	BS/STA-7.Z.1 high purity zinc	... 0.003		0.003	Total imp. incl. Cd and Pb 0.01% max.*			99.99
5.	BS/STA-7.Z.2 high grade zinc	...						99.95
6.	BS/STA-7.Z.3 zinc for rolling, foundry work, etc.	... 1.25	0.25					98.5
7.	BS/STA-7.Z.4 zinc for galvanising	... 1.6	0.08		Total other imp. 1.0% max.*			98.00
8.	BS. 1003 — 1942 high purity zinc	... 0.003		0.003	Other imp. excl. Fe and Cu traces. Total imp. 0.01% max.			Remainder

\* Impurities other than Pb, Cd, Fe, Cu—Traces only

Ref. : Thorpe's Dictionary of Applied Chemistry, Fourth Edition, Vol. XI, page 1067.

TABLE III ASTM B 6.46 specification for zinc : Chemical requirements

Sl. no.	Grade	Pb Max %	Fe Max %	Cd Max %	Pb+Fe+Cd Max %
1.(a)	Special high grade	0.006	0.005	0.004	0.01
1.	High grade	0.07	0.02	0.07	0.10
2.	Intermediate	0.20	0.03	0.05	0.50
3.	Brass special	0.60	0.03	0.50	1.0
4.	Selected	0.80	0.04	0.75	1.25
5.	Prime Western	1.60	0.08	—	—

Ref : Thorpe's Dictionary of Applied Chemistry, Fourth Edition, Vol. XI, page 1097.

starting raw material and as this does not dissolve in dilute  $H_2SO_4$ , it is converted into the soluble zinc oxide by roasting, the modern roaster being of the fluidised bed type. This zinc oxide together with the impurities is then leached in spent electrolyte solution till the required concentration of zinc and  $H_2SO_4$  are obtained by suitably adjusting the pH, etc. The leaching and purification steps are most intricate and are involved

in the entire process. The impure pregnant leach liquor is then purified to remove or control the undesirable or harmful impurities. The pure cell feed is fed to the electrolytic cells. Electrolysis of the purified solution is the most critical step of the process since this operation will react to impurities in amounts not readily detectable by ordinary means. Electrolytic zinc is recovered on a commercial scale by electrodepositing zinc from  $ZnSO_4$  solution in a cell using insoluble Pb-Ag anodes and high-purity aluminium cathodes. The mixture of depleted  $ZnSO_4$  and regenerated  $H_2SO_4$  formed during the electrolysis stage is returned to the leaching section to dissolve fresh quantities of calcine coming from the roaster. The whole operation being cyclic in nature, is highly susceptible to the build-up of impurities.

During the electrolysis of  $ZnSO_4$  solution, hydrogen and oxygen are evolved at cathode and anode respectively. The presence of these gases brings into play a factor known as over-voltage or polarization. From an examination of the electrode potentials, it would appear that metals baser than hydrogen in the scale could not be electrolytically precipitated, for, in each case hydrogen would be preferentially precipitated. In other words, it should be impossible to deposit zinc from an electrolyte containing  $ZnSO_4$  solution. The explanation lies in that the actual potential to deposit hydrogen at a zinc cathode is much higher than the theoretical value. The difference is called the hydrogen over-voltage (of a zinc electrode) which is of a very narrow margin and is calculated to be of the order of 0.05 V. The hydro-

TABLE IV Commercial grades of zinc (U. S. S. R. State standard)

Sl. no.	Designation			Min. Zn %	Max. impurities %							Total
					Pb	Fe	Cd	Cu	As	Sb	Sn	
1.	Zn	Grade B		99.99	0.005	0.003	0.002	0.001	—	—	—	0.01
2.	Zn	Grade O		99.96	0.015	0.010	0.010	0.001	—	—	—	0.04
3.	Zn	Grade 1		99.94	0.024	0.015	0.014	0.002	—	—	—	0.06
4.	Zn	Grade 2		99.9	0.05	0.04	0.02	0.002	—	—	—	0.1
5.	Zn	Grade 3		98.7	1.0	0.07	0.20	0.005	0.01	0.02	0.002	1.3
6.	Zn	Grade 4		97.5	2.0	0.15	0.2	0.05	0.01	0.02	0.05	6.5

Ref. : "General Metallurgy" Translated by B. Kuznetsov, Peace Publishers, Moscow, page 332.

gen over-voltage is due to the fact that hydrogen ions have a lower rate of discharge than zinc ions and anything causing even a slight lowering has detrimental effects during electrolysis. It is essential to reduce hydrogen production at the cathode for higher current efficiencies. To achieve this objective, concentrated electrolytes of the least possible acidity should be electrolysed at high current densities and low temperatures.

TABLE V I.S. specification for zinc : IS 209—1966 (Chemical composition)

Sl. no.	Item		Grade Zn 99.99 %	Grade Zn 99.95 %	Grade Zn 98.0 %
1.	Zinc	Min.	99.99	99.99	98.0
2.	Lead	Max.	0.003	0.03	1.6
3.	Cadmium	Max.	0.003	0.02	0.5
4.	Iron	Max.	0.003	0.02	0.05
5.	Tin	Max.	0.001	0.001	—
6.	Copper	Max.	0.002	0.002	—
7.	Thallium	Max.	0.001	—	—
8.	Indium	Max.	0.0005	—	—
9.	Total impurities	Max.	0.01	0.05	2.0

Ref. : Indian Standards Institution, New-Delhi IS : 209/1966, page 4.

### Impurities in the electrolyte

The ideal electrolyte would be an acid  $ZnSO_4$  solution containing no other elements, but in commercial practice the zinc electrolyte is relatively pure and should give a good deposit of zinc at high current efficiency.

Elements that are normally present and are detrimental to the successful operation of the electrolytic cell are : iron, cobalt, nickel, copper, arsenic, antimony, germanium, tin, selenium, tellurium, cadmium, lead, chlorine, fluorine and manganese.

Single element impurity can be detected by its effect on the deposit or action in the cell, but the effect of a combination of two or three elements is a tougher problem. Usually, a combination of detrimental elements is much more harmful than the same elements when present singly.

The impurities encountered in the electrolysis of zinc sulphate may be classified, according to their general effects in the cells, as cathodic impurities, anodic impurities and beneficial impurities.

### Cathodic impurities

The cathodic impurities can be further classified according to their effect on electrolysis :

- (i) Those metals whose sulphates decompose at a higher voltage than zinc sulphate : Al, Na, K, Mg, Mn.

These have no effects on electrolysis as far as reactions at the cathodes are concerned.

- (ii) Those metals whose hydrogen over-voltage is high enough not to cause the re-solution of zinc, but whose decomposition voltage is less than that of zinc : Pb, Cd.



TABLE VI Analysis of a few zinc concentrates of the world

Element	Tchibora pit % 2	Mozumi pit Kamioka mines Japan % 3	New Broken Hill Australia % 4	Mt. Isa Australia % 5	Zawar mines India % 6	Boudouin Burma % 7	Peru Brazil % 8	Calamine Iran (Calcined) % 9	Salfossa Italy % 10	Sardinia Italy % 11	Korea % 12	USA % 13
Zn	59.90	56.80	51.30	50.10	53.25	54.35	57.18	52.60	52.7	51.46	50.10	52.40
Fe	4.05	6.20	10.70	7.85	5.90	3.80	4.30	7.65	3.2	4.2	3.9	9.2
Pb	0.44	0.47	0.83	1.88	1.52	4.67	1.94	2.52	3.87	2.12	2.01	1.2
Cu	0.10	0.15	0.10	0.15	0.05	0.17	0.63	0.02	0.03	0.07	0.41	1.476
Cd	0.31	0.34	0.20	0.18	0.33	0.32	0.42	0.12	0.45	0.085	0.37	0.28
As	0.06	0.10	0.07	0.02	0.05	0.21	0.25	0.29	0.029	0.0230	0.0238	0.0168
Sn	0.0008	0.0009	Tr	0.002	0.0005	0.008	Tr	Tr	—	—	—	0.055
Sb	Tr	Tr	0.02	0.011	0.002	0.03	0.07	0.02	0.0057	0.0027	0.0010	0.0026
Bi	0.006	0.008	Tr	0.002	Tr	0.01	Tr	Tr	—	—	—	—
Ni	Tr	Tr	Tr	Tr	Tr	0.23	Tr	Tr	Tr	0.0032	0.0010	Tr
CO	0.015	0.018	0.015	0.006	0.007	0.04	Tr	Tr	0.0011	0.0004	0.0018	0.0112
SiO <sub>2</sub>	2.22	2.72	1.82	3.35	2.43	2.25	0.94	7.10	0.02	1.4	1.86	2.43
CaO	0.22	0.28	0.45	1.02	1.30	Tr	0.25	3.40	2.85	3.50	3.6	0.28
Al <sub>2</sub> O <sub>3</sub>	0.24	0.29	0.10	0.87	0.17	0.56	0.15	1.80	1.45	2.12	1.4	1.35
MnO	0.133	0.30	0.95	0.04	0.049	0.11	0.80	0.06	0.25 Mn	0.025 Mn	1.02 Mn	0.053 Mn
MgO	0.18	0.22	0.54	0.62	1.17	0.15	0.06	0.97	2.54	0.96	1.91	0.33
T-S	31.15	30.93	31.71	29.87	31.15	29.42	32.46	0.28	29.4	29.65	27.73	31.58
SO <sub>4</sub> -S	0.09	0.03	0.27	0.77	0.16	0.81	0.13	0.11	0.32	0.19	0.71	Tr
Cl	0.1	0.01	0.014	0.007	0.007	Tr	Tr	Tr	0.147	0.0098	Tr	Tr
Au (g/T)	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	—	—	—	—
Ag (g/T)	31	30	27	85	99	135	176	18	—	—	312	—
F	—	—	0.037	0.017	—	—	—	—	0.006	0.0083	0.0052	0.0045
Ge	—	—	—	—	—	—	—	—	0.0117	0.0047	Tr	0.0047

Ref. : Author's notes collected during the past few years.

These have no detrimental effect on the efficiency of zinc decomposition, but they do however deposit along with zinc and cause an impure product.

- (iii) Those metals whose hydrogen over-voltage is below that of zinc but whose decomposition voltage is above that of sulphuric acid : Fe, Ni, Co.

These metals are injurious to electrolysis but do not ordinarily contaminate the zinc deposit. They are soluble in acid and consume power by being alternately deposited on the zinc surface and re-dissolved in the acid electrolyte. They are particularly detrimental to electrolysis when present in combination with certain other impurities.

- (iv) Those metals of which the sulphate decomposition voltage is below that of  $H_2SO_4$  and the hydrogen over-voltage is low enough to cause re-solution of zinc : Cu, Ge, As, Sb.

This group is the most injurious of all impurities : they are deposited with the zinc and form points of low hydrogen over-voltage where hydrogen is evolved at the expense of zinc.

#### *Anodic impurities*

The anodic impurities include all the anions except those of  $H_2SO_4$ . The common ions of this group are : manganate, permanganate, chloride, chlorate, perchlorate and fluoride. Their effect on electrolysis is not so violent as that of the metallic impurities but they very often have a distinct bearing on the amount of corrosion occurring in the cell. Those anions which increase corrosion of Al-cathodes cause the deposited zinc "stick" to the Al-cathode. Sometimes this becomes so intense that the deposited metal has to be removed only by dissolving in acid. Those anions which increase corrosion of Pb anodes cause an increase of Pb in the zinc deposits.

#### *Beneficial impurities*

These include all those addition agents : glue, manganese. They are normally used to prevent more detrimental effects of certain other impurities. Glue is used to increase the hydrogen over-voltage and to give a hard smooth zinc deposit. Manganese is used to protect anode from corrosion.

#### *Effect of impurities*

##### *Antimony*

This is one of the most injurious impurities. Zinc becomes spongy and dark in colour. Better purification, lower temperature and shorter deposition time will reduce these detrimental effects.

However, a small amount of antimony, it appears, has been found beneficial when there is an unusual amount of cobalt in the electrolyte.

Besides, addition of small quantities of soluble antimonates facilitates the removal of cathode deposits.

##### *Arsenic*

This is less injurious than antimony. Its presence is detected when pronounced corrugation of the zinc surface with absence of usual lustre of the deposit and sprouts and leads on the deposit are observed. Its presence indicates the presence in solution of antimony and germanium.

##### *Cobalt*

Cobalt is the most serious impurity but its detrimental effects are not so violent as those of antimony. Besides, its removal is more difficult.

Cobalt will cause round holes in the deposits and also cause re-solution of the zinc deposit. Its detrimental effect is increased by the presence of germanium and to a less degree by higher acid concentration.

Although cobalt lowers current efficiency, its presence in the electrolyte in controlled amount has a beneficial influence in lowering the amount of lead in the zinc deposit.

An addition agent consisting of glue, beta-naphthol and antimony is added to the electrolyte in order to prevent the loss of large amounts of cobalt.

##### *Germanium*

This metal causes a multitude of pin holes in the deposit which tend to overlap, resulting in spongy metal or large areas burned away.

This has a tendency to build up in the system and with the presence of Co or Sb is very detrimental even when present in very minute quantities.

##### *Nickel*

This has somewhat the same effect as cobalt. Its presence makes the zinc deposit to re-dissolve and also contaminates the zinc metal.

##### *Copper*

Copper is easily removed by ordinary purification methods. It is introduced in the electrolysis section by the corrosion of copper header bars.

Its presence in the electrolyte results in severe resolution of the zinc deposit and also contaminates the zinc metal. It also corrodes the Al cathode sheets.

##### *Cadmium*

Cadmium has no deleterious effect on current efficiency but only contaminates the zinc metal. It appears that cadmium in small amounts has been claimed to increase the ampere efficiency. It is easy to reduce the cadmium content in the solution, but it may be extremely difficult to eliminate it completely.

### Lead

The greatest source of lead in the zinc cell is from corrosion of the lead anodes or lead lining of the cells by impurities like chlorine, fluorine. It also contaminates the zinc metal due to the suspension of lead compounds in the electrolyte during electrolysis.

### Iron

The presence of iron indicates that other impurities that are precipitated along with iron may also be present. The alternate oxidation and reduction of iron at anode and cathode respectively consumes power and thus ampere efficiency is reduced. Small amounts of iron in the electrolyte inhibits the deposition of lead in the zinc deposit.

### Manganese

Manganese is usually considered a harmless impurity. In large quantities it causes the zinc to form a rough spongy deposit with many beads and sprouts. Manganese deposits at the anode during electrolysis as  $MnO_2$ . Low acidity, low temperature and low current density cause heavy anode coatings. Large quantities of  $MnO_2$  in the electrolyte may contaminate the zinc deposit with lead and also increase the cell voltage. A certain amount of impurities may also be removed from the electrolyte through absorption in it.

### Chlorine

In small quantities, chlorine does not materially affect ampere efficiency. Chlorine contributes to the presence of lead in the zinc deposit due to corrosion of the anode. It also affects the corrosion of aluminium. If large quantities are present, the zinc deposits tend to adhere tightly to the Al-cathode.

### Fluorine

Fluorine has been recognized as the chief contributor of the zinc deposit 'sticking' to the Al-cathode, sometimes so tightly that its removal by ordinary means becomes impossible.

The chief method of combating fluorine is by conditioning the cathode, to prevent corrosion, in spent electrolyte containing a little aluminium sulphate.

### Nitrates

Nitrates have the same effects as chlorides. Corrosion of lead is increased and the amount of lead deposited with zinc is larger when nitrates are present.

### Tin

Appreciable amounts of tin cause a lowering of hydrogen over-voltage and ampere efficiency. Tin causes a marked increase in the lead content of the zinc deposit. Tin rarely appears in the electrolyte. Concentrates containing high tin are considered unfavourable.

### Selenium

Large amounts of selenium cause severe re-solution of the zinc deposit.

### Tellurium

Small amounts of tellurium have the same effect as selenium; tellurium is especially harmful in the presence of cobalt.

### Sodium, potassium, calcium, aluminium, magnesium

When present in normal amounts, these usually have no particular effect on ampere efficiency or on the

TABLE VII Average analysis of blende used in zinc smelter, Debari

Month (1968)	Moisture %	Zn %	Fe %	S %	Cl ppm	F ppm	Pb %	Cu %	Cd %	Co %	Ni %
January	2.10	53.50	6.40	30.50	14	—	1.12	0.04	0.40	0.0008	0.0003
February	1.99	53.99	6.05	30.06	16	—	1.02	0.05	0.32	0.0012	0.0005
March	2.13	54.20	5.67	30.17	16	60	1.12	0.07	0.30	0.0041	0.0004
April	2.71	53.70	5.70	30.67	15	63	1.02	0.06	0.27	0.0035	Tr
May	2.54	52.60	5.67	30.05	17	65	1.03	0.07	0.29	0.0030	Tr
June	2.06	53.73	5.60	30.38	17	72	1.22	0.05	0.31	0.0029	0.0006
July	3.02	53.50	5.47	29.93	16	60	1.09	0.04	0.33	0.0021	0.0010

Ref.: Monthly reports of the Laboratory, Zinc Smelter, Debari.



TABLE VIII Average analysis of calcine from the roaster at zinc smelter, Debari

Month (1968)	Total Zn %	H <sub>2</sub> SO <sub>4</sub> Soluble %	Zn Solubility %	Total Fe %	H <sub>2</sub> SO <sub>4</sub> Soluble Fe %	Total S %	SO <sub>4</sub> -S %	H <sub>2</sub> S-S %	Pb %	Cu %	Cd %	Cl ppm	F ppm	Co %	Ni %
January	61.39	56.50	91.95	7.50	1.02	3.59	3.10	0.49	1.21	0.05	0.47	Tr	—	0.0010	0.0044
February	61.75	57.27	92.74	6.86	0.73	3.60	3.17	0.43	1.16	0.06	0.38	Tr	40	0.0015	0.0006
March	62.11	57.40	92.57	6.26	1.14	3.87	3.50	0.37	1.29	0.08	0.35	Tr	70	0.0050	0.0005
April	61.53	57.20	92.96	6.34	1.09	3.80	3.47	0.33	1.16	0.07	0.29	Tr	78	0.0040	Tr
May	60.67	56.77	93.55	6.32	1.17	3.69	3.33	0.36	1.27	0.08	0.36	Tr	83	0.0040	Tr
June	61.93	58.12	93.85	6.48	1.14	3.46	2.99	0.47	1.42	0.06	0.34	Tr	90	0.0038	0.0008
July	61.11	56.66	92.71	6.33	0.97	3.09	2.74	0.38	1.19	0.06	0.34	Tr	75	0.0030	0.0013

Ref.: Monthly reports of the Laboratory, zinc smelter, Debari.

nature of the deposit. But some of these elements are cumulative, and if they build up to large amounts they may become detrimental. For example, when Mg concentration goes beyond certain limits, the electrolyte is to be discarded at intervals so as to keep the Mg concentration within satisfactory limits.

#### Removal or control of impurities

Removal, control or elimination of impurities is effected right from the selection of concentrates up to the melting and casting of the zinc ingots.

#### Selection of concentrates

As far as possible, concentrates with minimum impurities should be selected to avoid difficulties at the purification and electrolysis stages of the process. Concentrates high in arsenic, germanium, etc. are rejected (Table VII).

#### Roasting stage

Roasting has considerable influence on the amount of certain impurities left in the calcine. Temperature and time are important factors. The elements that are particularly eliminated or controlled during roasting are fluorine, chlorine, sulphur, selenium and tellurium. Selenium and tellurium may be volatilized to a considerable extent but they may reappear in the flue dust. Sulphur is removed by conversion to oxide chlorine which is removed by volatilization. Fluorine is also removed under the same conditions, but elimination of fluorine is improved by an increase in roasting time and temperature and adequate exposure of the material to the roasting atmosphere. Elements normally of concern during roasting are iron, lead and bismuth. High iron content in the concentrates may form insoluble zinc ferrites. High lead content requires extra precautions in roasting to avoid the loss of lead through volatilization. Excess of bismuth is rarely encountered but with high content of bismuth, this may be reduced to the metallic form within the furnace to the extent that roasting is prevented (Table VIII).

#### Leaching stage

The elements barium, silver, gold, lead and bismuth are normally insoluble in dilute H<sub>2</sub>SO<sub>4</sub> and hence do not create any problem in their removal.

Precipitation of ferric hydroxide assists in the removal of other impurities like arsenic, antimony, germanium, etc. that are much more difficult to eliminate. Prolonged time, increased temperature and neutral pH will facilitate this reaction to take place and improve the elimination of the impurities (Table IX).

Manganese, cobalt, nickel, fluorine and chlorine are rarely precipitated to any extent in the iron purification step.

Tellurium is precipitated here if present in quadri-valent state. Selenium is partially precipitated. Silicon is brought under control by iron precipitation.

The elements tin, gallium, indium, thallium and

TABLE IX Average analysis of neutral overflow at zinc smelter, Debari

Month (1968)	Zn g/l	Co mg/l	Ni mg/l	Cu mg/l	Cd mg/l	Fe mg/l	As mg/l	pH	Sb mg/l
January	131.8	2.07	1.30	46	563	Tr	Tr	5.5	—
February	133.7	2.20	0.78	47	428	Tr	Tr	5.4	—
March	133.9	2.65	0.95	43	419	Tr	Tr	5.5	—
April	133.3	2.85	1.02	39	422	Tr	Tr	5.5	0.055
May	124.1	2.24	1.35	39	467	Tr	Tr	5.5	0.018
June	129.5	2.63	1.50	38	430	Tr	Tr	5.6	—
July	126.9	2.41	1.90	42	516	Tr	Tr	5.6	0.062

Ref. : Monthly reports of the Laboratory, zinc smelter, Debari.

mercury are usually present in extremely small amount. They are reduced in amount to such an extent that further purification steps are not necessary.

Chlorine may be removed on the basis of precipitation of nearly insoluble chlorides of copper, silver or mercury. If sufficient silver is present, chlorine is removed as silver chloride. But copper purification is used in most cases, the reagent being freshly deposited cement copper.

TABLE X Average analyses of first and second purification filtrates at zinc smelter, Debari

Month (1968)	First purification				Second purification	
	Co mg/l	Ni mg/l	Cu mg/l	Cd mg/l	Co mg/l	Ni mg/l
January	1.77	0.5	Tr	3.30	0.21	0.22
February	1.75	Tr	Tr	2.55	0.38	Tr
March	2.08	Tr	Tr	2.64	Tr	Tr
April	2.59	Tr	Tr	2.27	0.007	Tr
May	2.84	Tr	Tr	1.95	0.31	Tr
June	2.38	Tr	Tr	2.30	0.11	Tr
July	2.21	0.39	Tr	2.17	0.12	Tr

Ref. : Monthly reports of the Laboratory, zinc smelter, Debari.

### Purification stage

#### (a) First purification

The elements copper, cadmium, nickel, germanium, arsenic and antimony are normally controlled in the first zinc dust purification step.

Cadmium is quite easy to remove but it has a tendency to re-dissolve, especially if the solution is aerated during purification and filtration. Several methods are used to avoid the re-solution of cadmium, such as (i) the addition of an excess of zinc dust just prior to filtration, (ii) by making the purification in two or more stages. Ferric sulphate and free acid in the filtered neutral overflow will dissolve precipitated cadmium. (Table X).

#### (b) Second purification

Cobalt is precipitated by any of the following methods : (i) by addition of potassium antimony tartrate, (ii) by addition of nitroso-beta-naphthol, (iii) by addition of an aqueous solution of sodium ethyl xanthate, or (iv) by a hot copper-arsenic zinc dust purification step (Tables X and XI).

#### (c) Other elements

Sodium, potassium, calcium and magnesium may be present in large amounts without any detrimental effects.

Calcium may cause serious trouble through precipitation of gypsum in pipe-lines and other equipment but is limited in its solubility.

Magnesium can build up to a point where it inter-



TABLE XI Average analysis of cell feed at zinc smelter, Debari

Month (1968)	Zn g/l	Acid g/l	Ce mg/l	Ni mg/l	Cu mg/l	Cd mg/l	Fe mg/l	As mg/l	Mn g/l	Cl <sup>-</sup> mg/l	T-Cl <sub>2</sub> mg/l	F mg/l	Mg g/l
January	132.8	0.80	0.20	0.2	Tr	1.80	1.0	0	0.35	21	70	9	2.79
February	134.0	1.39	0.47	Tr	Tr	2.62	Tr	0	0.37	—	55	16	6.63
March	140.2	0.70	0.67	Tr	Tr	2.57	Tr	0	0.52	2	41	16	7.48
April	132.5	1.85	1.12	Tr	Tr	3.36	Tr	0	0.55	3	50	16	7.90
May	122.9	5.70	1.13	Tr	Tr	1.85	Tr	Tr	0.86	3	—	17	8.07
June	129.1	1.34	0.95	Tr	Tr	2.11	Tr	Tr	1.15	29	—	16	11.00
July	127.2	0.90	0.95	Tr	Tr	2.20	Tr	Tr	1.25	48	—	16	—

Ref. : Monthly reports of the Laboratory, zinc smelter, Debari.

feres with the solubility of zinc. A special purification step, consisting of an acid leach on the unroasted concentrates is an effective method of controlling magnesium. At some plants magnesium is controlled by discarding the electrolyte at intervals, in order to keep the magnesium content within the desired limits.

Selenium and tellurium are normally within the limits. Any excess of tellurium will appear along with the MnO<sub>2</sub> sludge formed at the anodes. To control tellurium, this sludge should therefore be discarded instead of sending it back to the system to oxidise iron at the leaching stage.

#### Electrolysis stage

The harmful effects of some impurities may be moderated by the addition of colloids like glue or goulac to the electrolyte. They also increase the hydrogen over-voltage and thus increase the quality of the deposit and ampere efficiency.

Beta-naphthol is used alone or in conjunction with glue as an addition agent.

Addition of strontium or barium carbonate to the electrolytic cell will materially reduce the amount of lead deposited with zinc.

Addition of manganese in the electrolyte in small quantities protects the anode from corrosion. The average analysis of spent electrolyte is given in Table XII.

The mist of oxygen and acid from the cells may be effectively kept down by the addition of a mixture of cresylic acid, sodium silicate and gum Arabic to the electrolyte which forms a froth on the solution. This will incidentally prevent corrosion of copper header

TABLE XII Average analysis of spent electrolyte at zinc smelter, Debari

Month (1968)	Zn g/l	Acid g/l	Mn g/l	Ni mg/l	Cl <sup>-</sup> mg/l	T-Cl <sub>2</sub> mg/l	F mg/l
January	57.6	115.0	0.04	0.04	2	63	—
February	64.0	115.0	0.05	Tr	Tr	49	14
March	95.4	113.7	0.09	Tr	1	32	16
April	61.1	112.0	0.10	Tr	2	45	15
May	58.9	108.0	0.41	Tr	2	—	13
June	61.1	110.0	0.66	Tr	18	—	15
July	58.5	112.0	0.66	Tr	39	—	15

Ref. : Monthly reports of the Laboratory, zinc smelter, Debari.

**TABLE XIII** At-random analysis of zinc ingots at zinc smelter, Debari

Sl. no.	Pb g/t	Cu g/t	Cd g/t	Fe g/t	Zn (by diff.) %
A	190	35	40	60	99.9675
B	241	22	21	78	99.9638
C	227	30	27	25	99.9691
D	270	45	22	20	99.9643
E	256	45	30	15	99.9654
F	200	18	20	80	99.9682
G	210	40	35	40	99.9675
H	225	28	50	15	99.9682

Ref. : Daily reports of the Laboratory, zinc smelter, Debari.

bars from acid spray and thus reduce the copper content in the zinc cathodes. An at-random analysis of zinc ingots, produced at the Debari Zinc Smelter, is given in Table XIII.

### Conclusion

Various impurities in the zinc concentrates and electrolytes, their effect and removal or control at different stages of the plant have been described in a general way. It will be appreciated that every plant has its own system of purification depending on the impurities present. It is earnestly hoped that this short and brief coverage of such a difficult subject will be a starting point for more information to be made available to the infant Indian electrolytic zinc industry about the effect of impurities in the production of electrolytic zinc.