

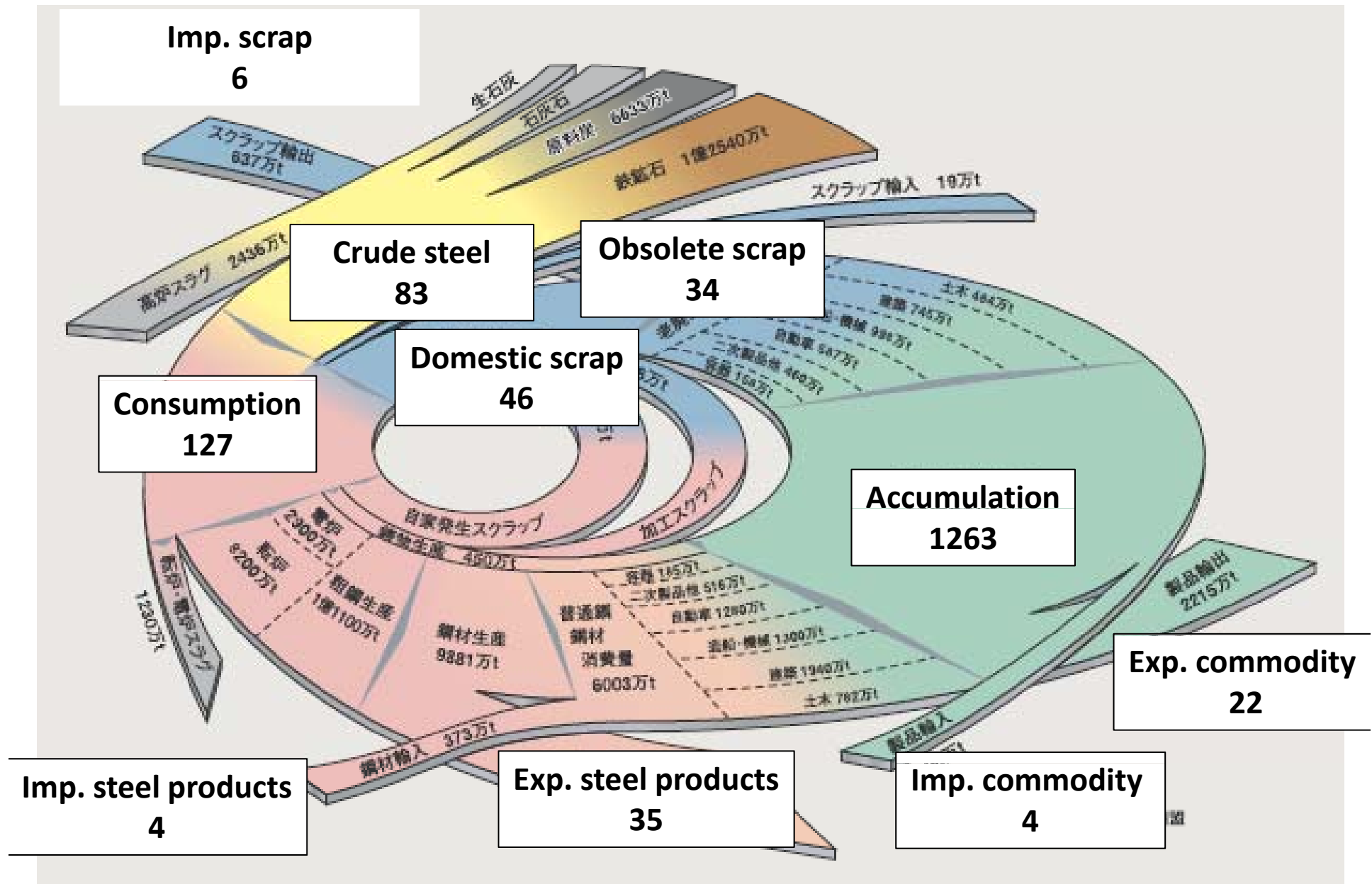
Steel Recycling and Reutilization of Alloying Elements

K. Matsubae-Yokoyama and T. Nagasaka
Tohoku University, Sendai, Japan

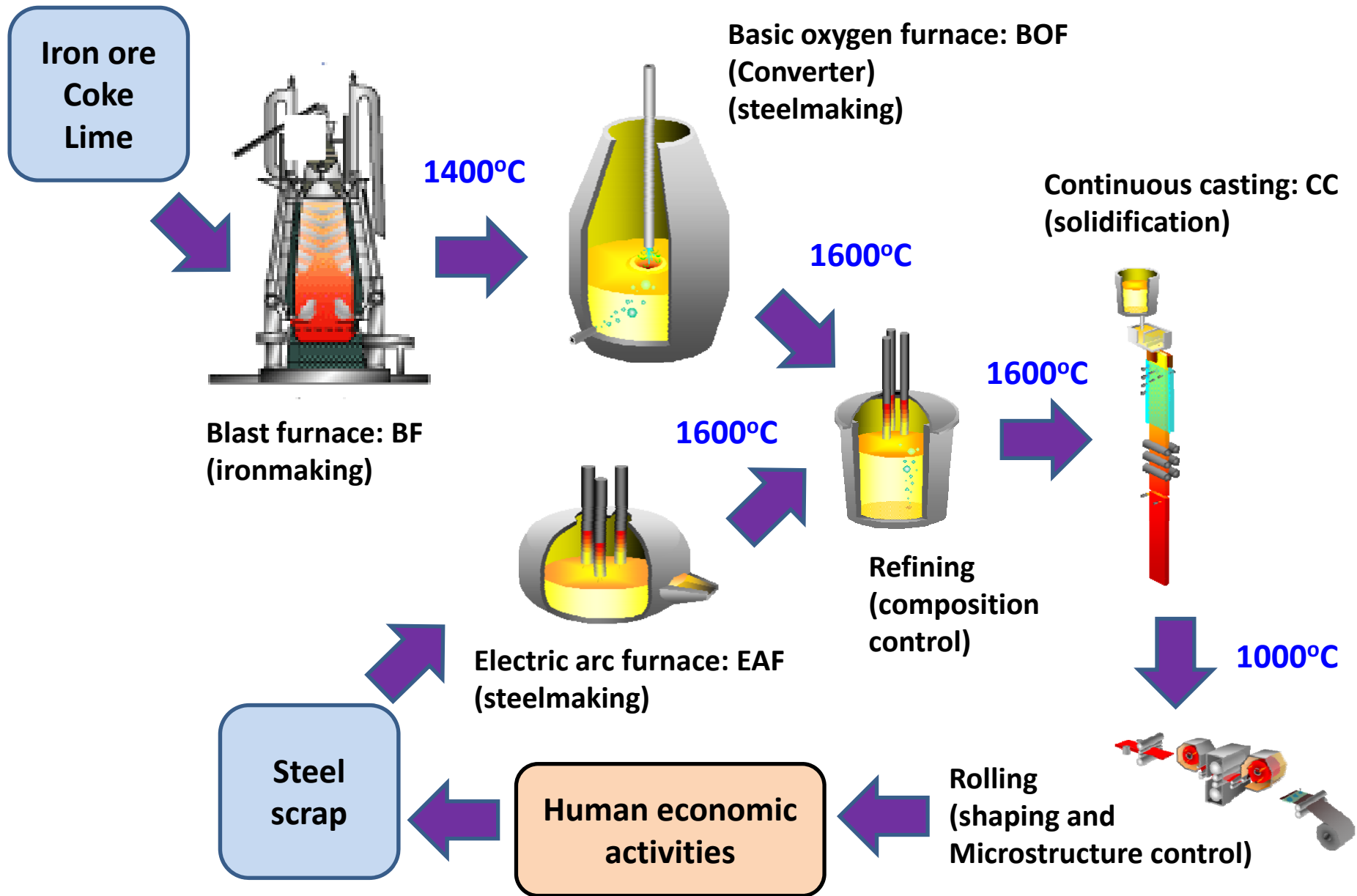


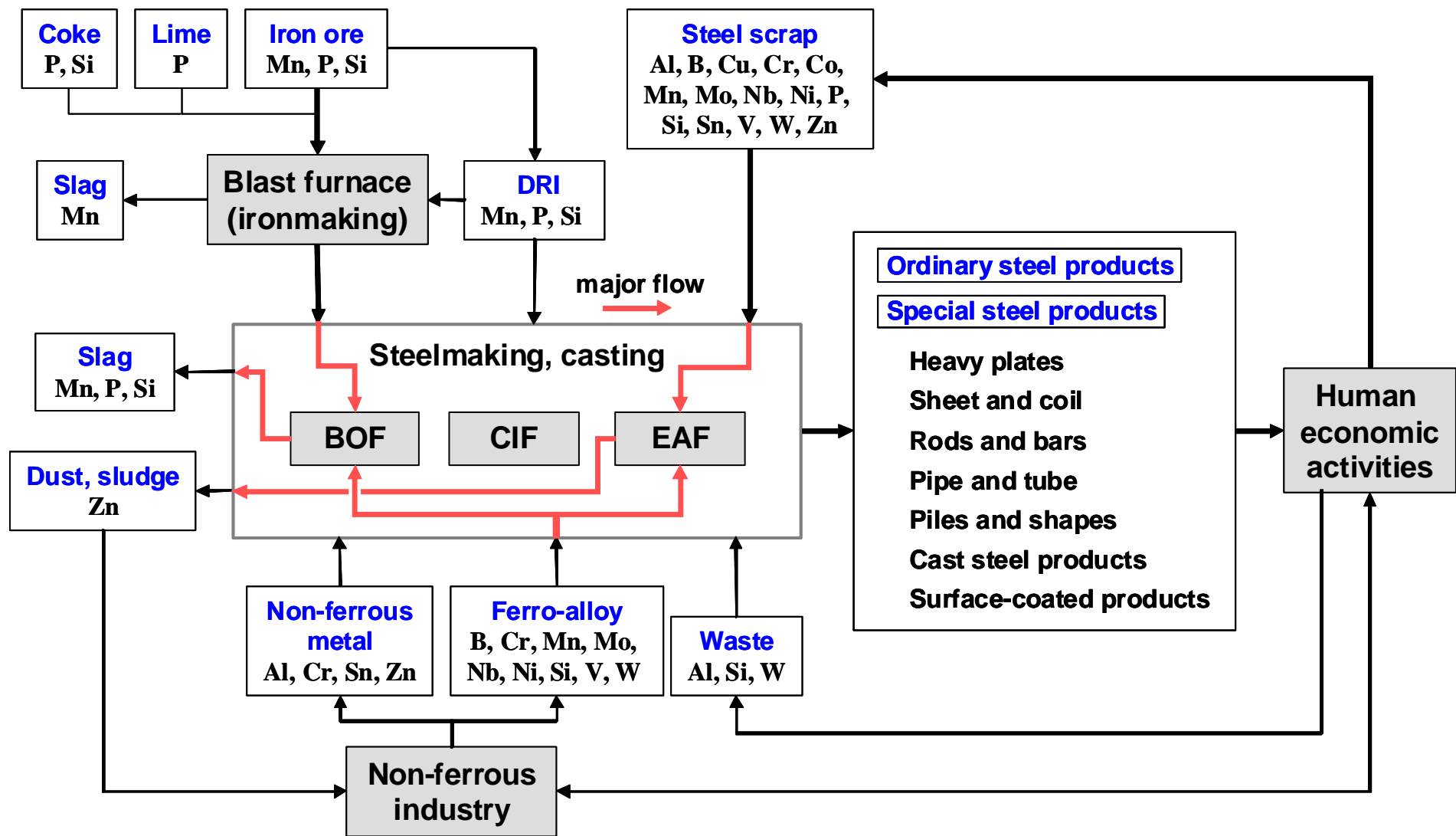
TOHOKU
UNIVERSITY

Iron and steel cycle in Japan (2003) source:JISF



Iron and steelmaking process





Rare metals in the life-cycle of steel products

We have three major concerns for the sustainable steel recycling

1) Contamination by or loss of alloying elements, which are mostly important resources, in the usage of steel scrap as iron resource

Development of “scrap soating system based on composition”

2) Significant loss of valuable elements into slag during steel refining processes

Development of “slag-making technology” to recover P, Mn and Cr

3) unefficient intermediate process for dust treatment

Development of “dust-making technology” to recover Zn

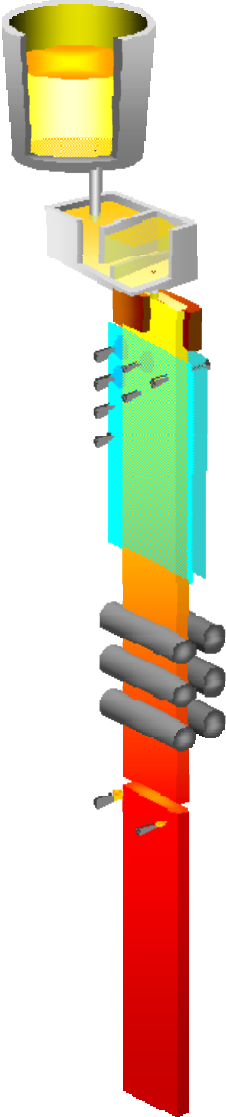
Classification of rare metals used in steel

T. Nagasaka: Study on global flow of Metals- An example of material recycling -, Report of ISIJ (2008)

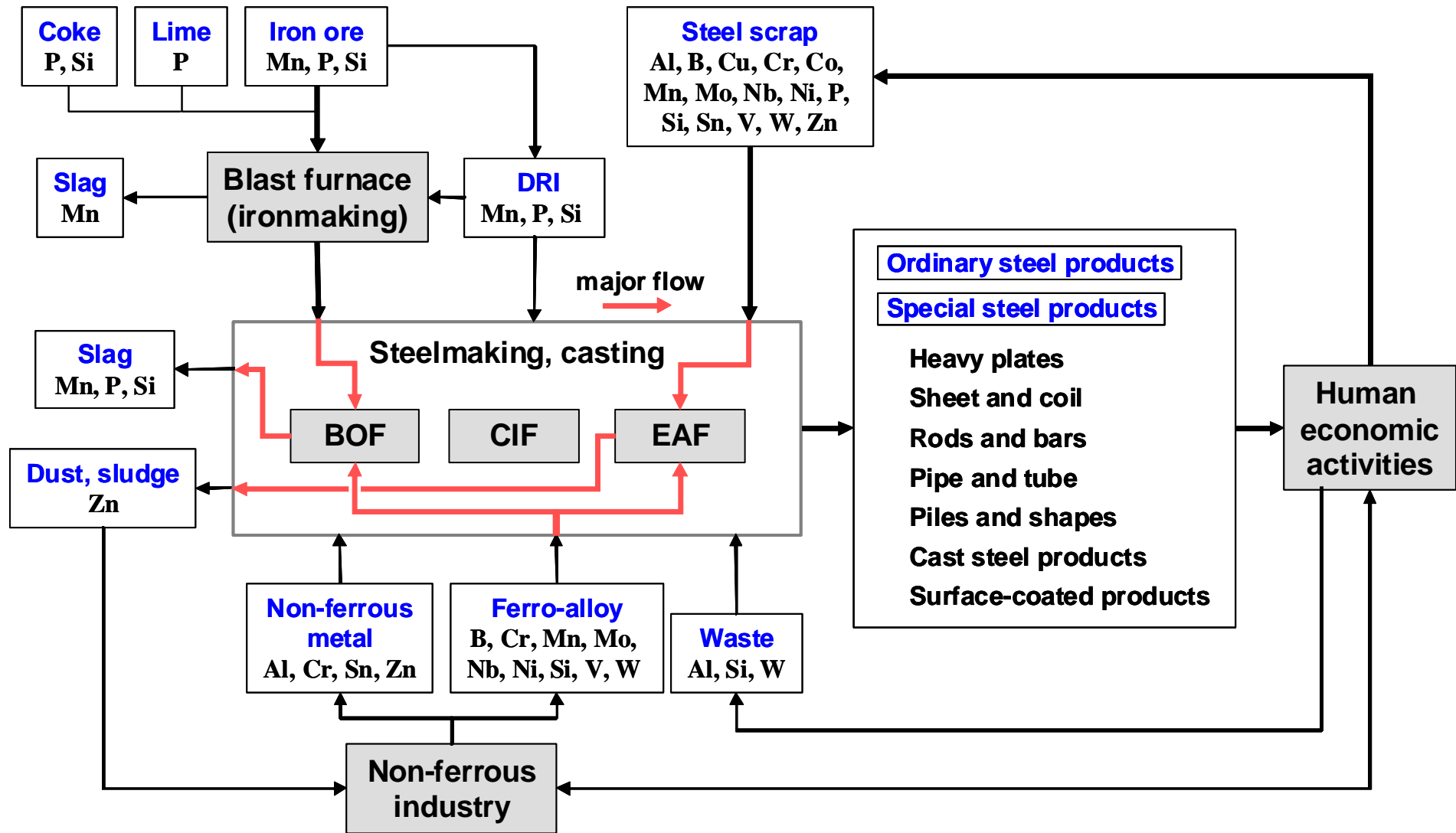
| type | Element | | | |
|---------------------|-----------|------------|-----------|----------|
| Well-used | Fe | C | | |
| Passed through | Si | P | S | |
| One way diffusion | Mn | Mo | Nb | V |
| Partial circulation | Cr | Ni | | |
| Waste accepted | W | Al* | Zn | |

MFA is done in Tohoku
 * including dross

Red: concentrated one in steel industry



What about "scrap-soating"?



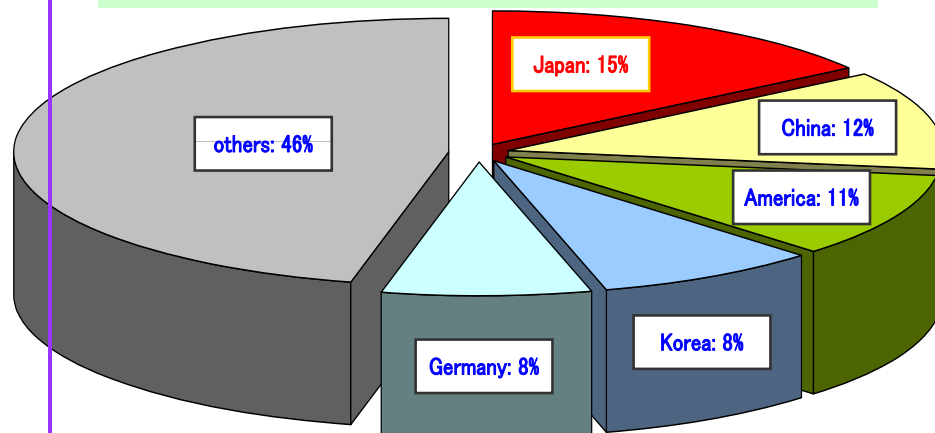
Rare metals in the life-cycle of steel products



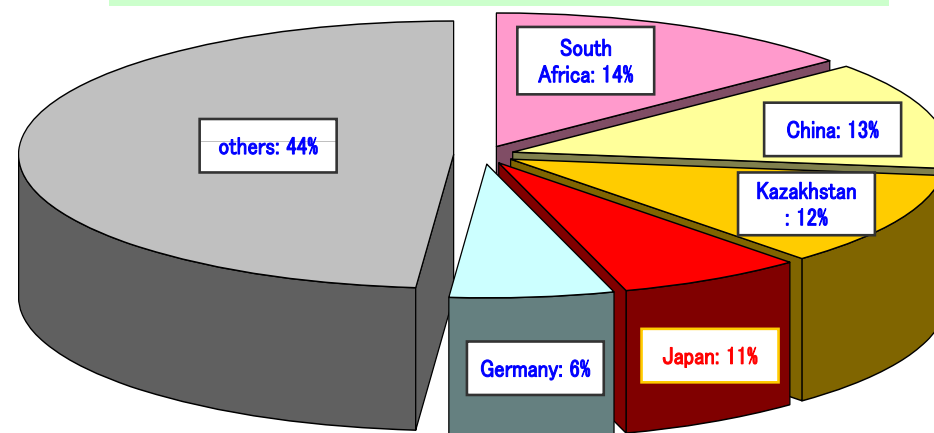
Demand of rare metals in the world

Large amount of rare metals are consumed in Japan. On the other hand, it is expected to **increase consumptions** of rare metals **in other Asian countries** (China, Korea...) with industrial development.

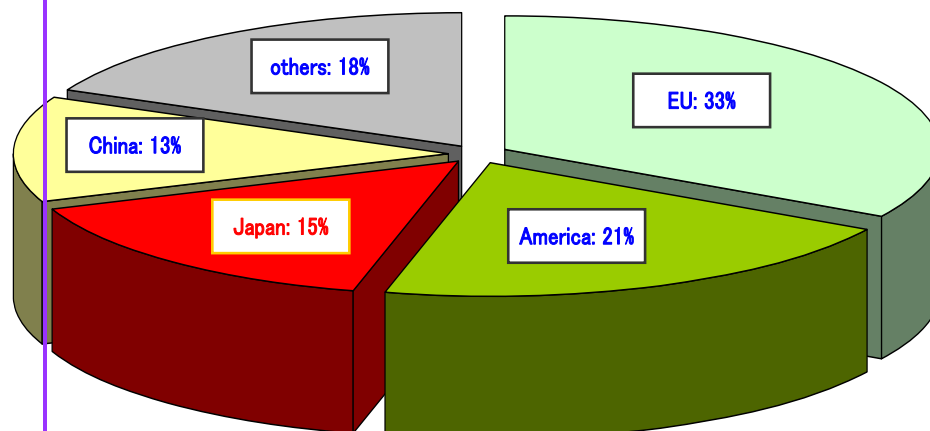
(a) Ni, Consumption(World) :
 $1,253 \times 10^3$ Ni-t (2004)



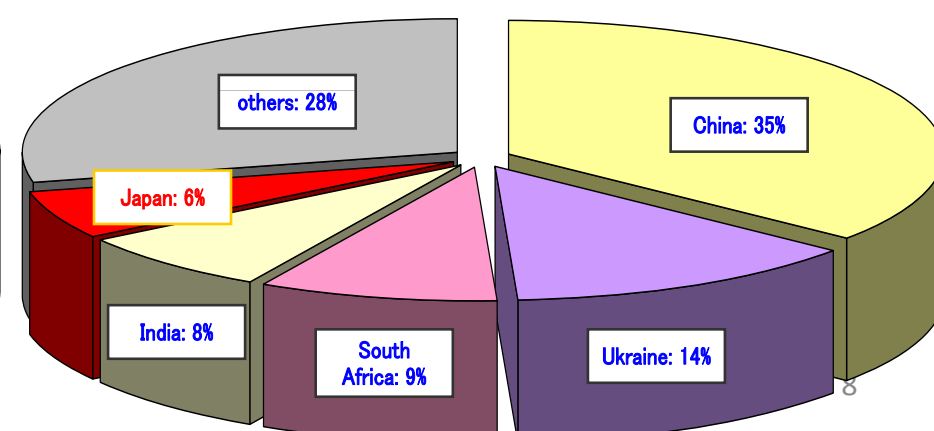
(b) Cr, Consumption(World) :
 $4,695 \times 10^3$ Cr-t (2003)



(c) Mo, Consumption(World) :
 175×10^3 Mo-t (2004)



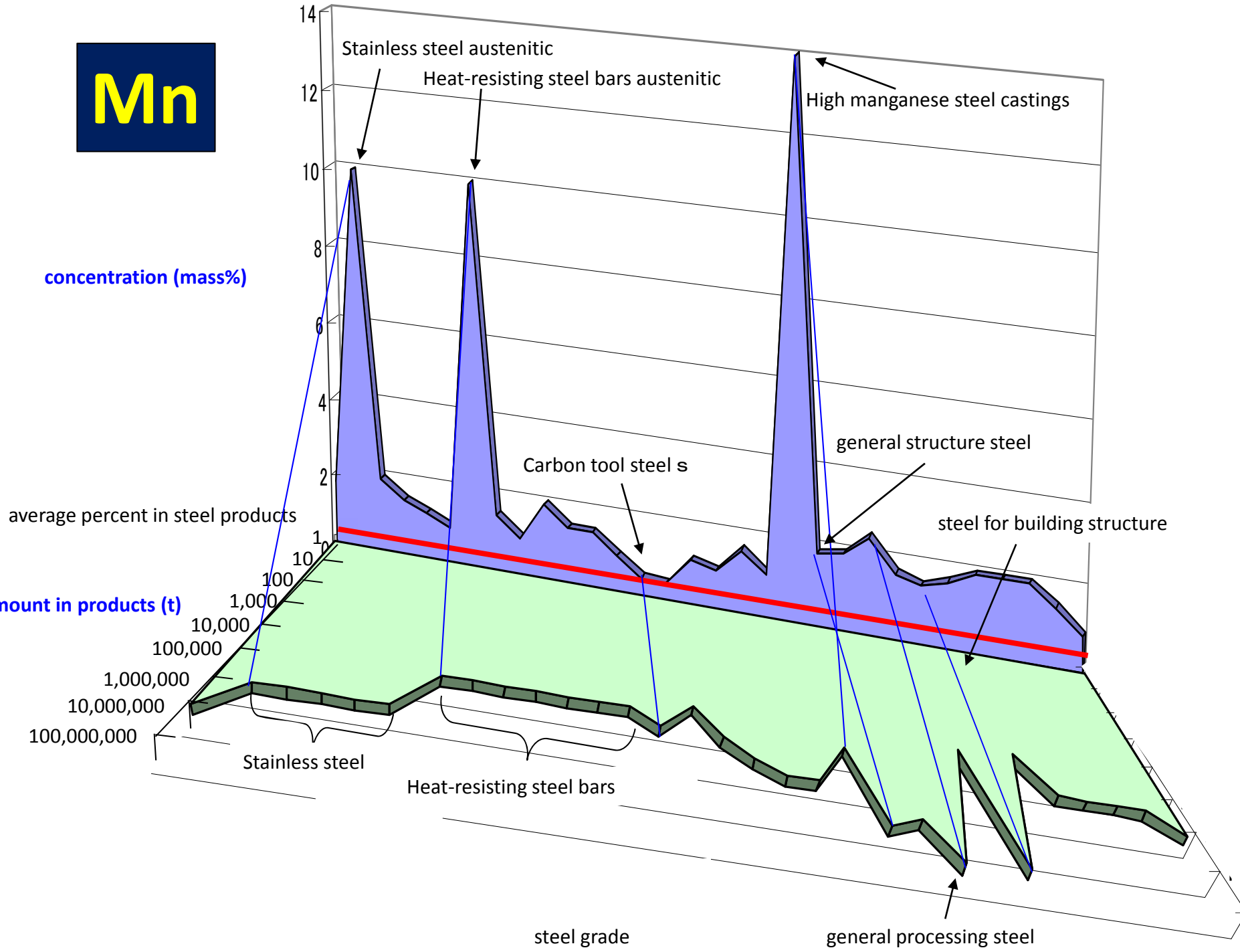
(d) Mn, Consumption(World) :
 $19,630 \times 10^3$ t (2001)



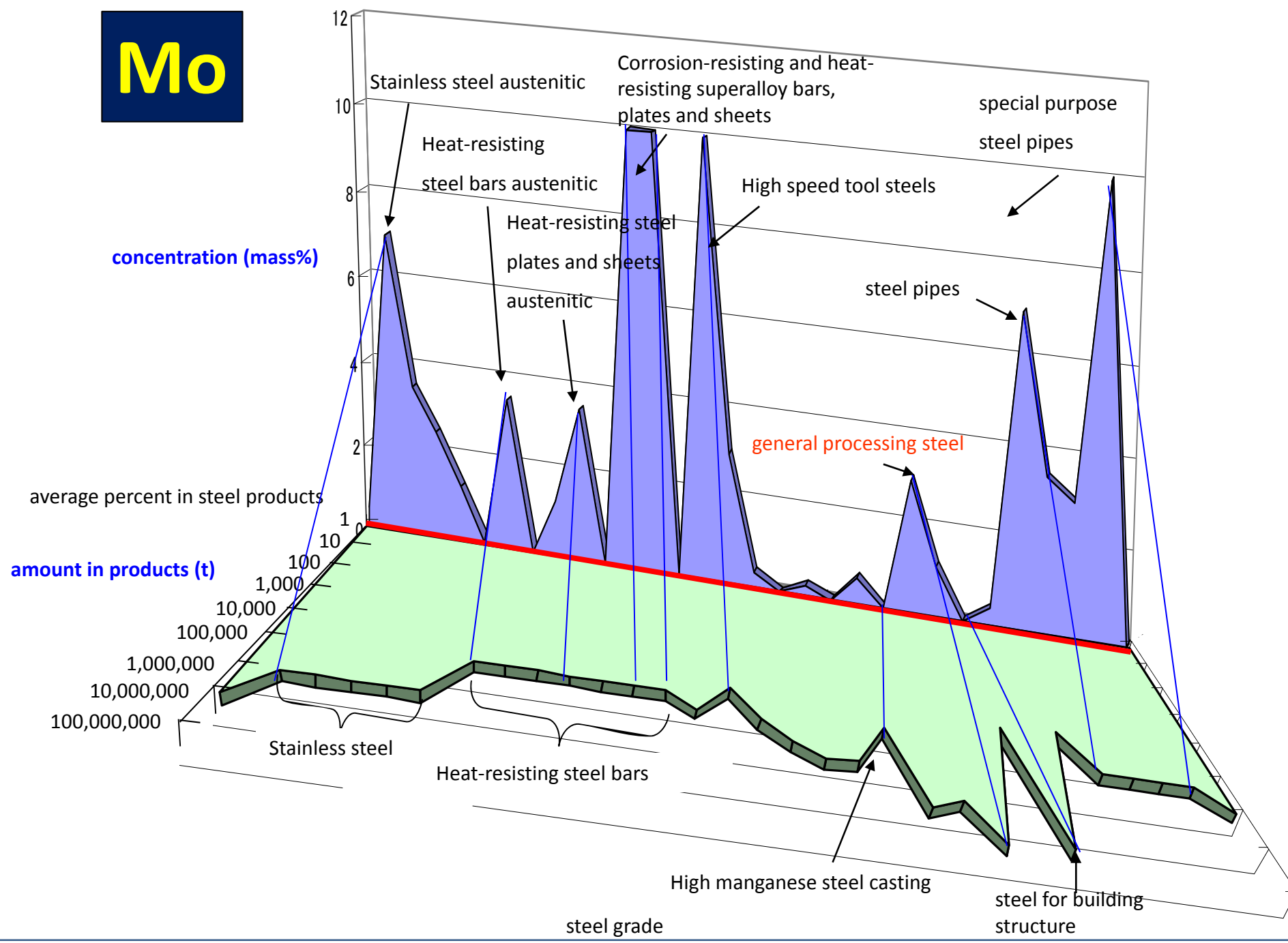
Mn

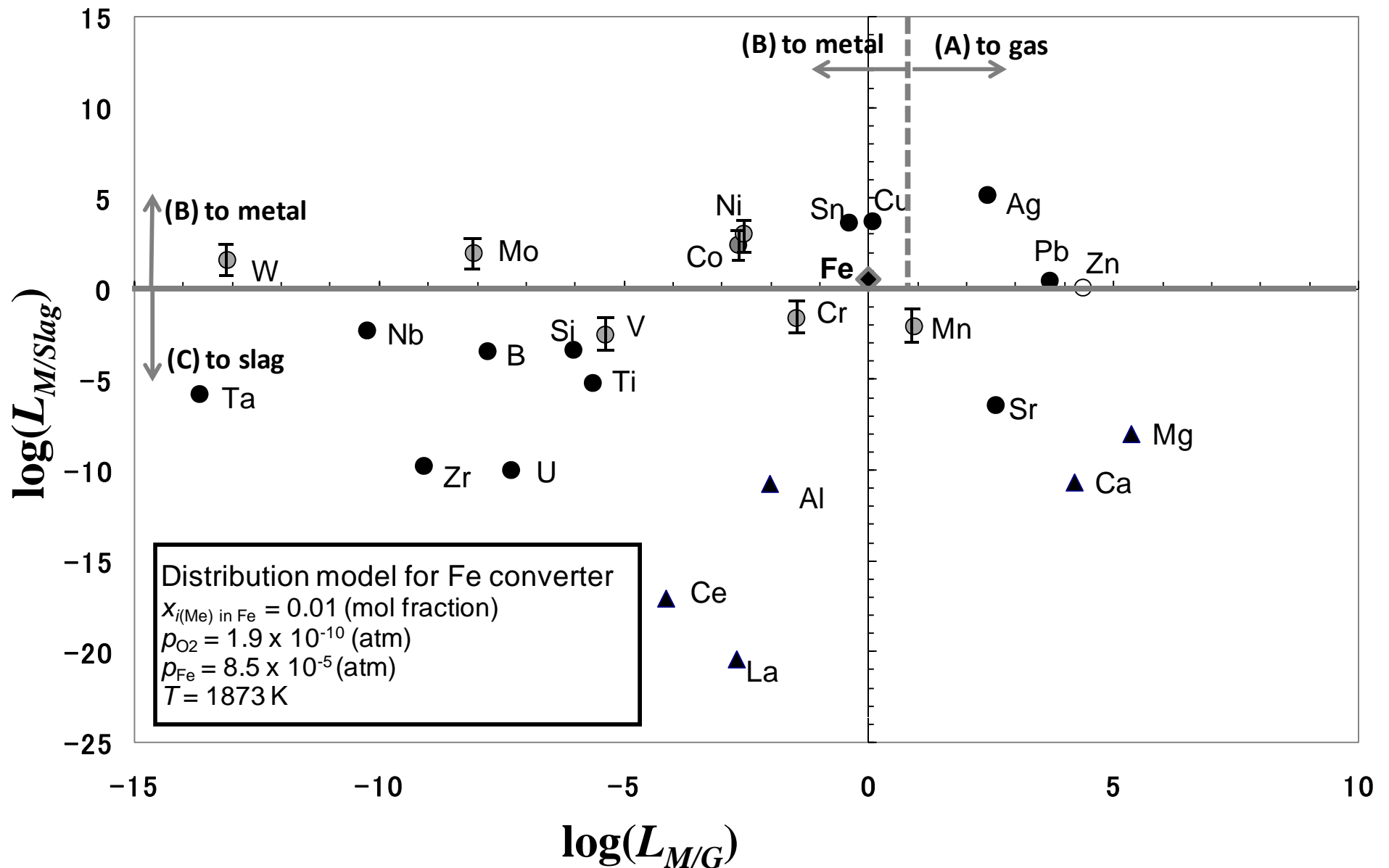
concentration (mass%)

amount in products (t)



Mo





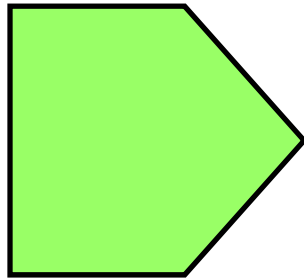
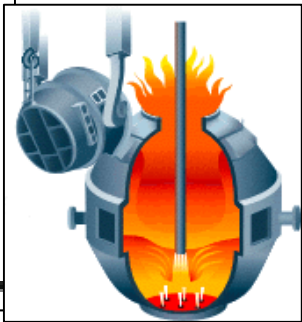
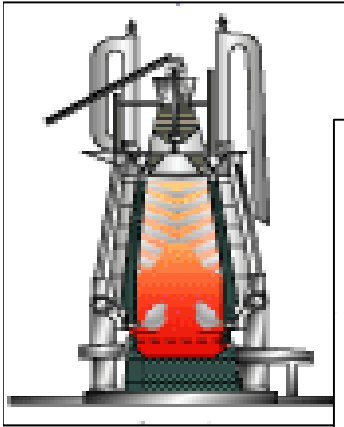
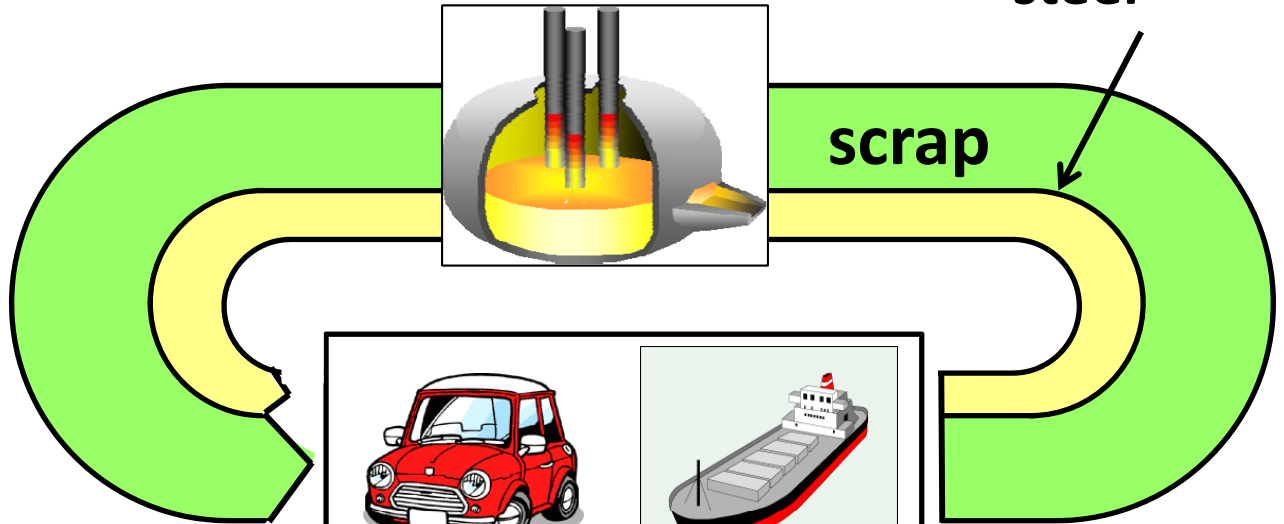
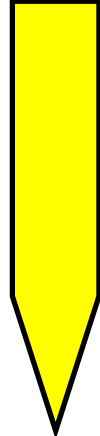
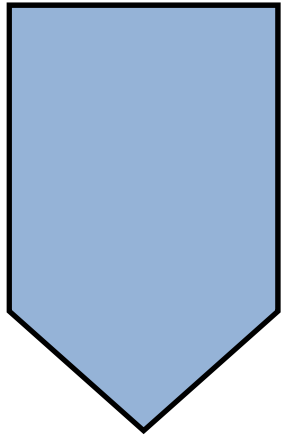
Distribution chart of elements among gas, slag, and metal phases for the metal recovery under the simulated atmosphere of converter of steel making.

Iron ore

Ferro alloy

Electric Arc Furnace (EAF)

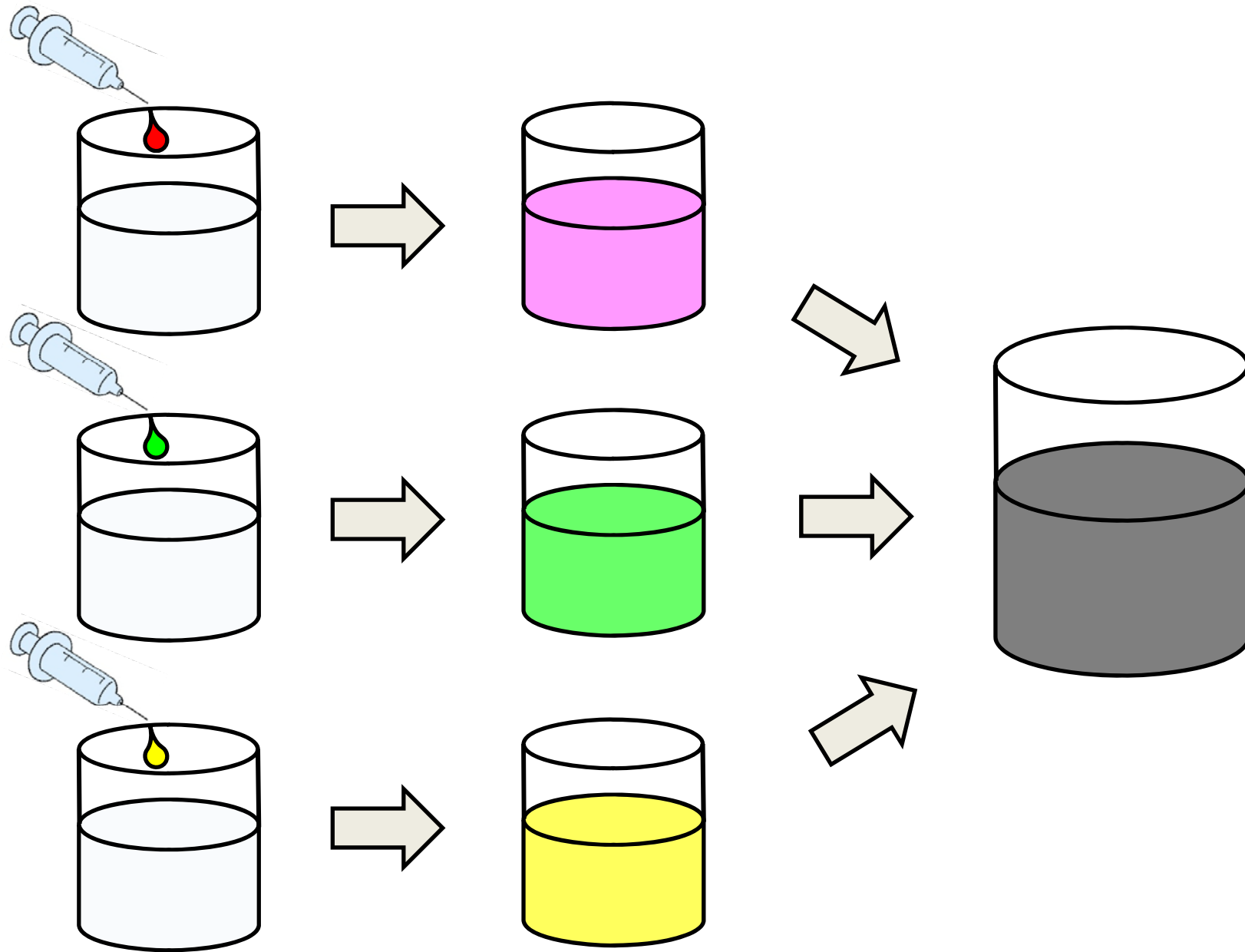
Stainless steel



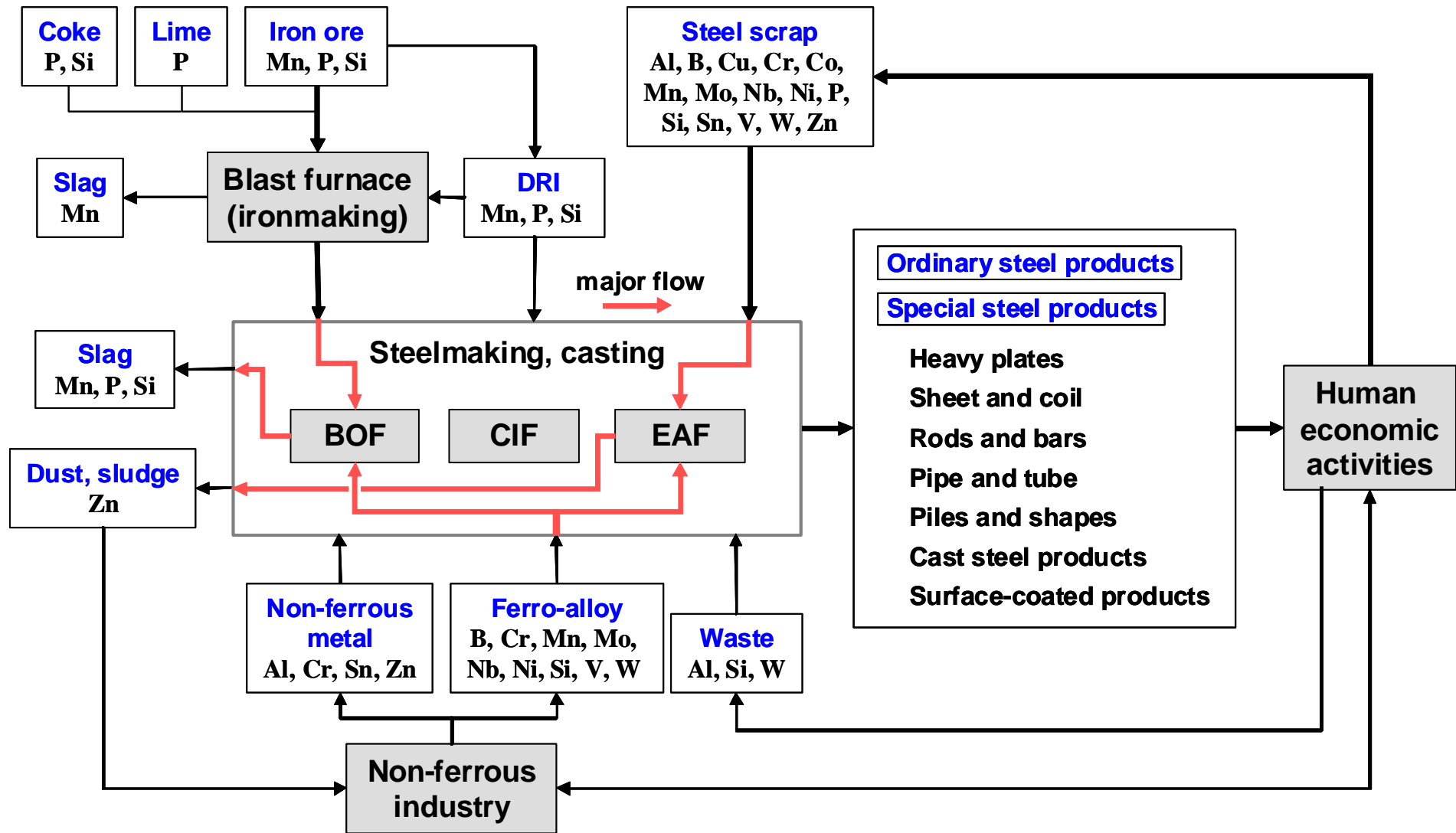
Human economic activities

**Blast Furnace (BF)-
Converter (BOF)**

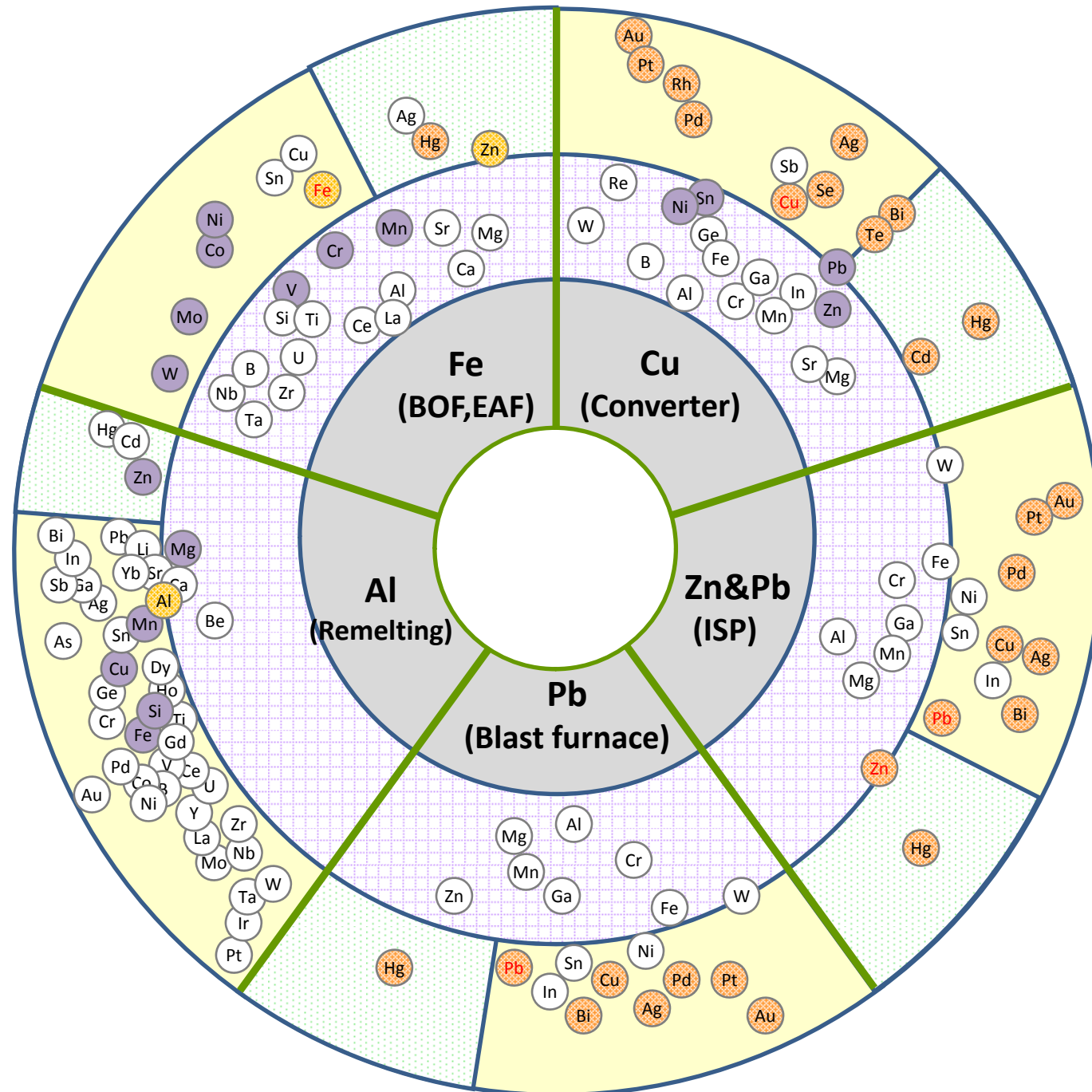
Present situation of steel recycling



What about "slag-making technology" ?



Rare metals in the life-cycle of steel products



to Metal phase

Elements that have distributed among the metal phase as a solid or liquid metal

to Slag phase

Elements that have distributed among the slag phase as oxide

to Gas phase

Elements that have evaporated and distributed among the gas phase .

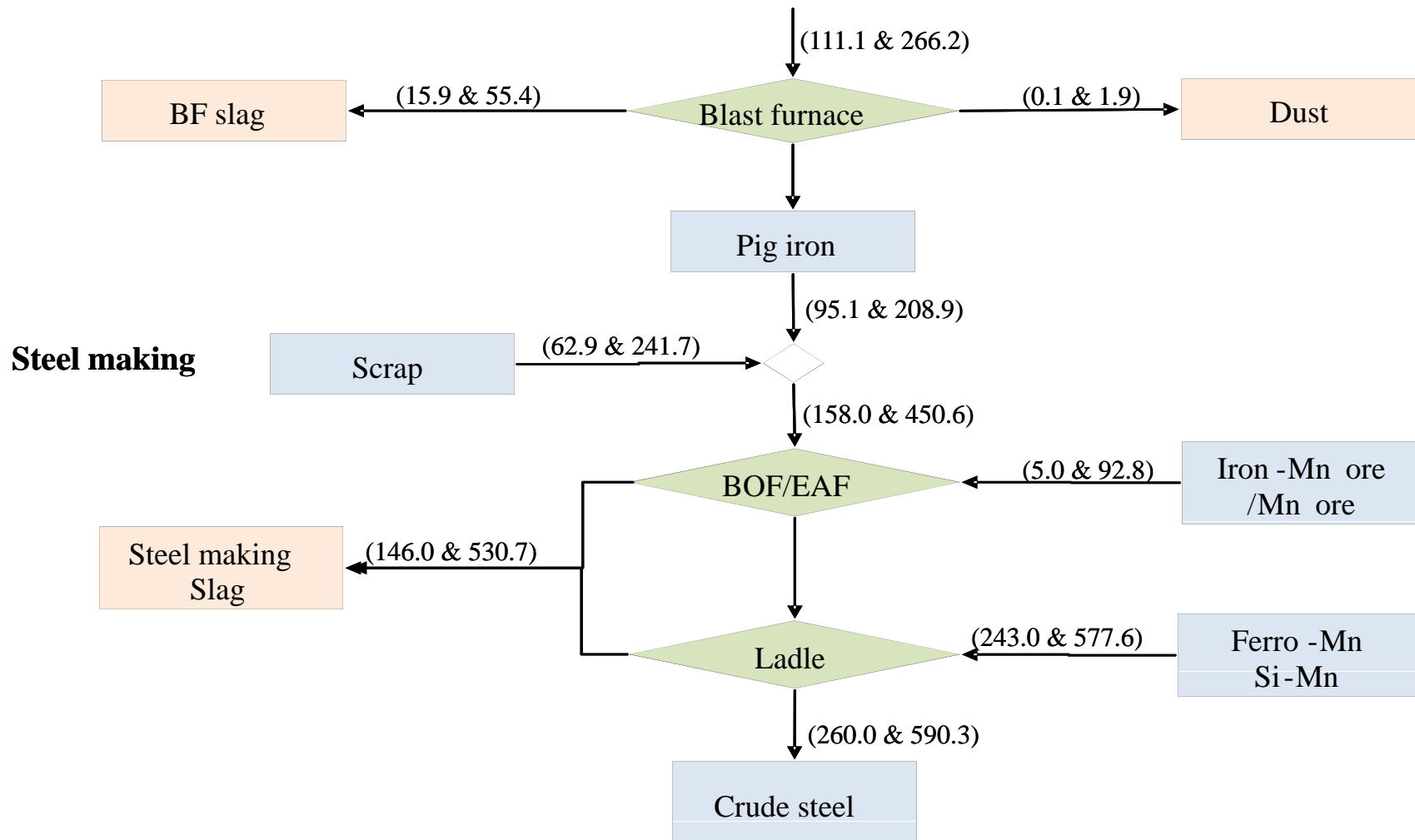
- Recyclable element
- Alloying element

Element distribution metal wheel

Iron making

Ferrous resource

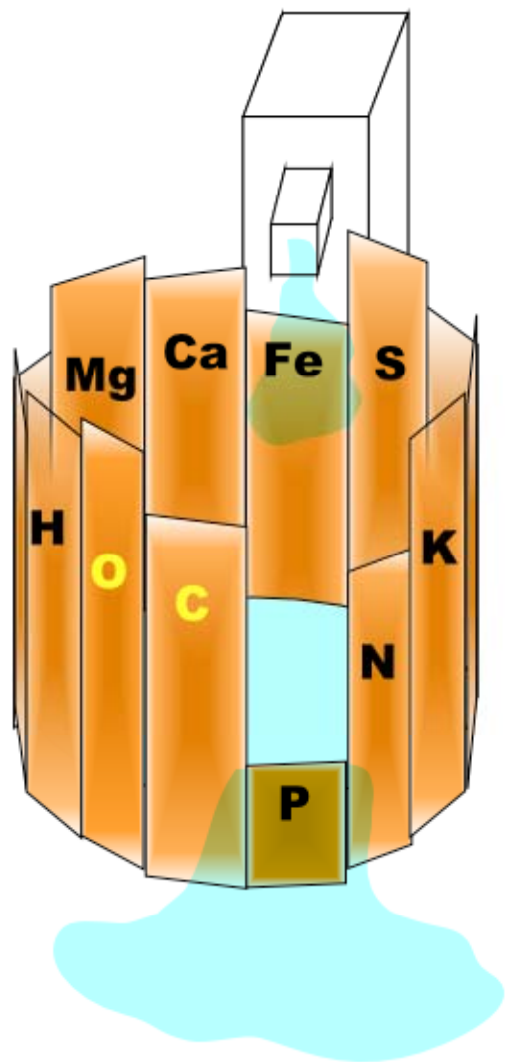
Unit: kt-Mn/year (South Korea & Japan)



Material flow of manganese in Japanese and South Korean steel industries (2005)

Why Phosphorus . . . ?

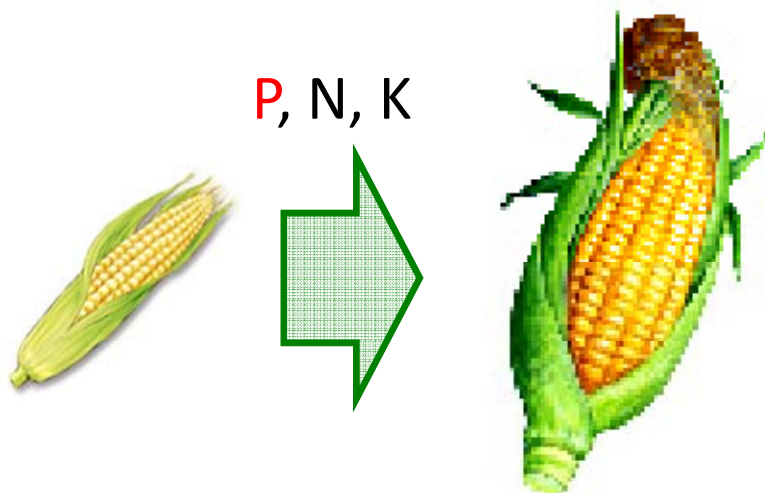
An essential element for animals and plants nutrition.



Supply of **P** often becomes critical for growth of plants

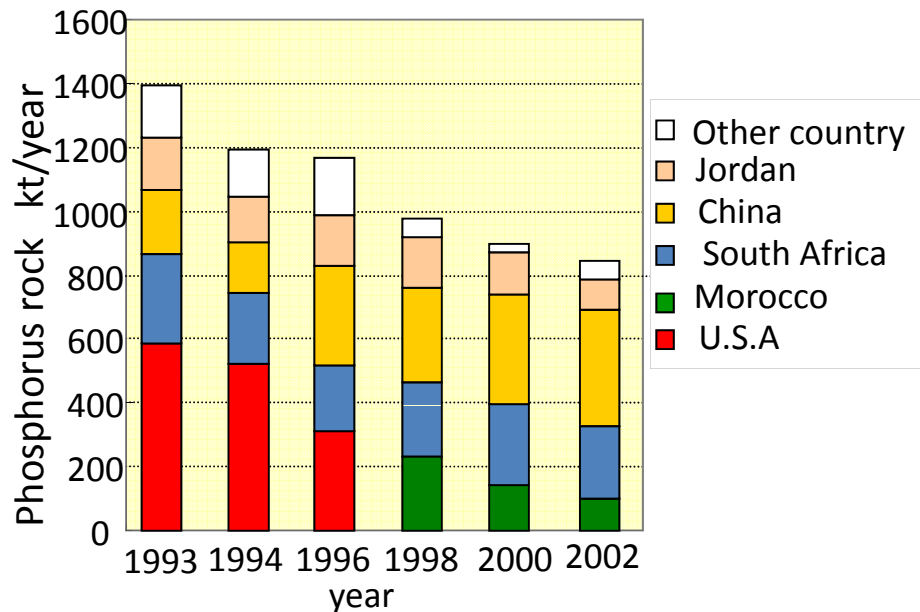
Nutrition barrel

Water level in the barrel, which is determined by the shortest plate, means growth degree of plant.



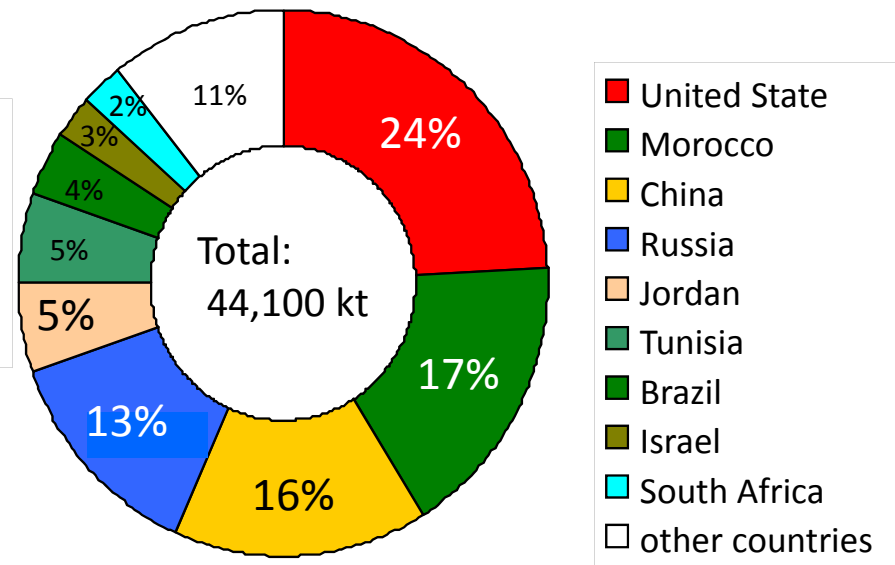
About Phosphorus • • •

- Domestic production: none (import only!)
- Main use: raw materials of fertilizer



Quantity about phosphorus ore import.

Ministry of finance Japan "Trade Statistics"



Phosphorus rock production rate in the world. (2002)

Phosphorus ore is a kind of national strategic resources

Trend in EU

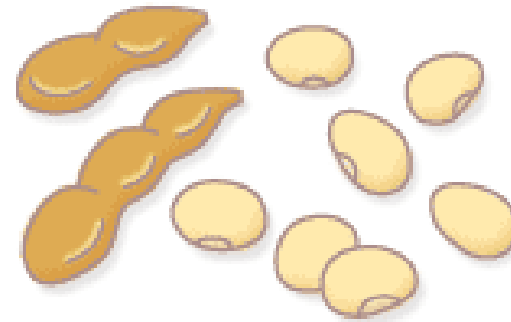
(reported by European commission in 2000)

Situation seems to be same in EU!

(1000 t, 1995)

| | USA | FSU* | Morocco | Algeria | Tunisia | Jordan | Israel | Togo | S. Africa | Other |
|----------|-------|-------|---------|---------|---------|--------|--------|-------|-----------|-------|
| Austria | | | 65.2 | 4.8 | 12.8 | 20.5 | 10.3 | | | 48.0 |
| Belgium | 190.8 | 158.4 | 514.2 | 20.5 | 17.6 | | | | 629.1 | |
| Denmark | | 67.3 | 6.4 | 11.8 | | 5.5 | | | 15.5 | 33.0 |
| Finland | | 91.3 | | | | | | | | |
| France | | 16.9 | 212.7 | 110.9 | 196.5 | | 646.3 | 103.3 | | 199.9 |
| Germany | 78.7 | 22.2 | 66.4 | | | 67.5 | 14.6 | | | |
| Greece | | | 19.3 | 91.4 | 5.3 | 155.4 | | 75.9 | | 131.1 |
| Ireland | 0.4 | | 10.0 | | | | | | | |
| Italy | | | 202.7 | | 3.0 | | 13.8 | | | 44.0 |
| Netherl. | 269.0 | 483.6 | 276.2 | | | 447.6 | 290.1 | | 20.9 | 88.0 |
| Portugal | | | 6.0 | | 22.9 | | | | | 128.0 |
| Spain | | | 1624.4 | 13.2 | 18.2 | | | 54.3 | | 49.0 |
| Sweden | | | 70.5 | | | | | | | 5.0 |
| UK | | 11.9 | 8.2 | 10.4 | | | | | | |
| Total EU | 538.9 | 851.6 | 3082.2 | 263.0 | 273.3 | 696.5 | 975.1 | 233.5 | 665.4 | 721.0 |

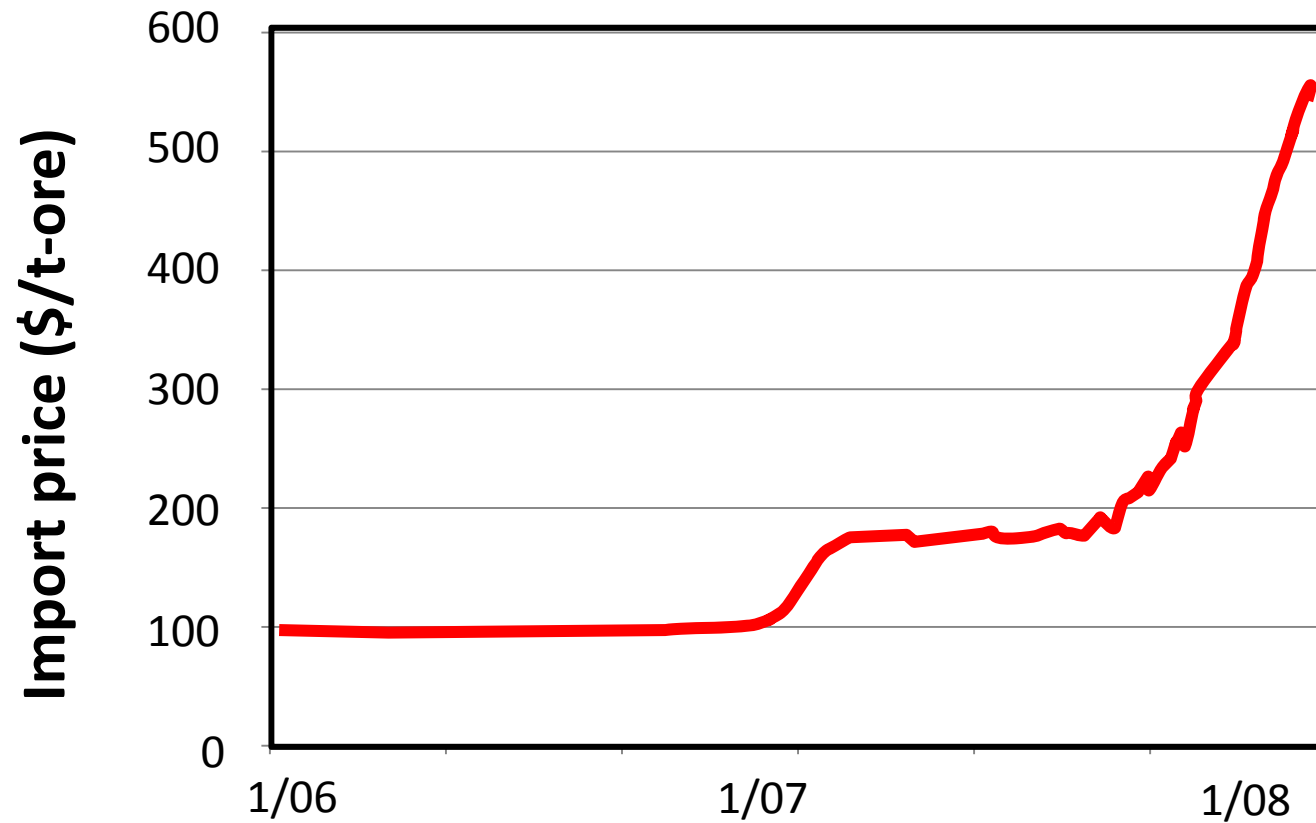
Trend in other country



Brazil was phosphorus exporting country

But now they are importing phosphorus due to bio-fuel production

Trend of *price of phosphate rock*



Phosphorus problems

Efficiency of phosphorus as fertilizer strongly depends on the composition of soil and kind of crop

Phosphorus is unsubstitutable element for plants and crops

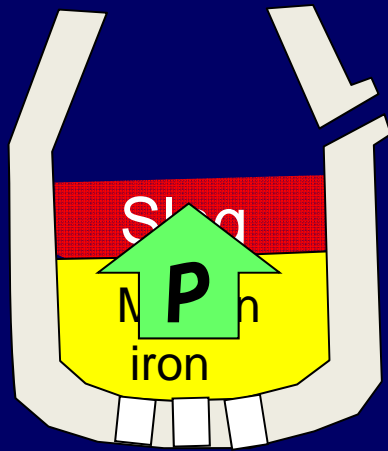
Phosphorus deposits are in very limited area

Phosphate rock mining sometimes causes water pollution

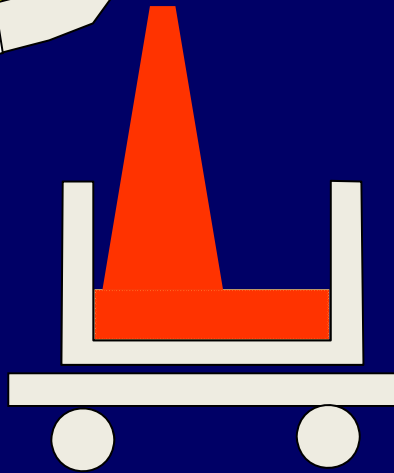
Supply of phosphorus strongly links to the production of food and bio-fuel

What's de-P process?

BOF or TPC



Ladle



Phosphorus is a kind of natural enemy for steel product

One of the main objectives of steel-making process is "dephosphorization"

before 0.1~0.15%P

after 0.02~0.01%P

Typical de-P flux

CaO-FeO-SiO₂-P₂O₅ system



Phosphorus and the Titanic

K. Felkins, H.P. Leighly, Jr., and A. Jankovic:

The Royal Mail Ship Titanic: Did a Metallurgical Failure Cause a Night to Remember?
Journal of Metals, 50 (1) (1998), pp. 12-18.

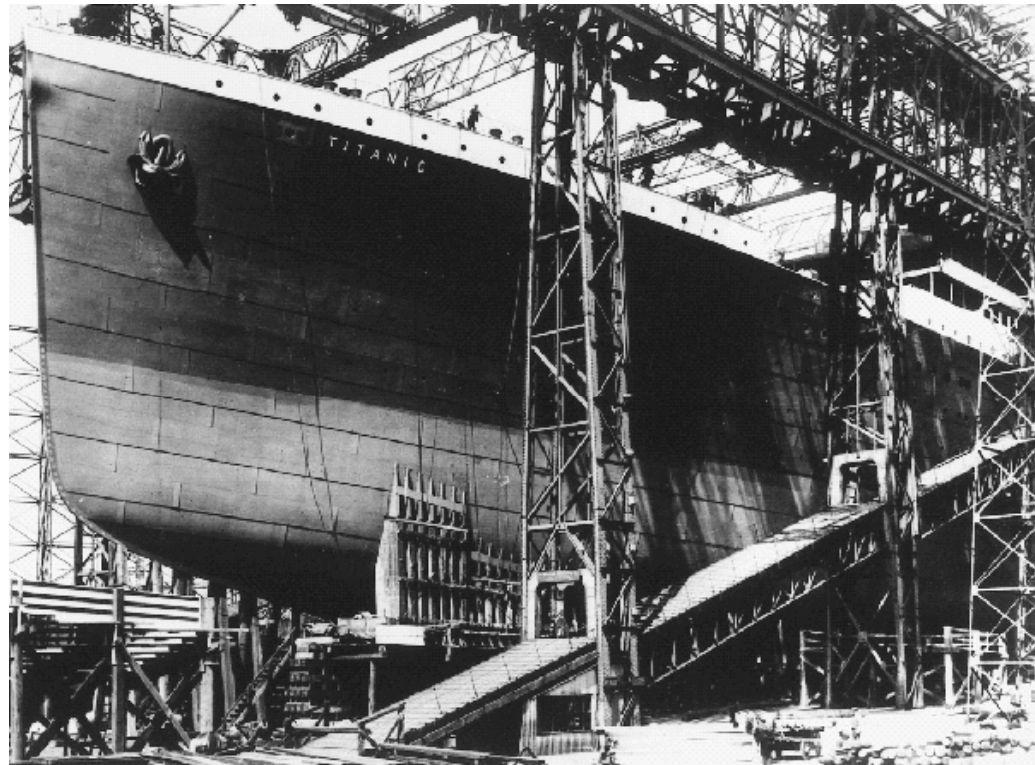


Figure 1. The Titanic under construction at the Harland and Wolff shipyard in Ireland. (Photo courtesy of the Titanic Historical Society.)

Phosphorus and the Titanic

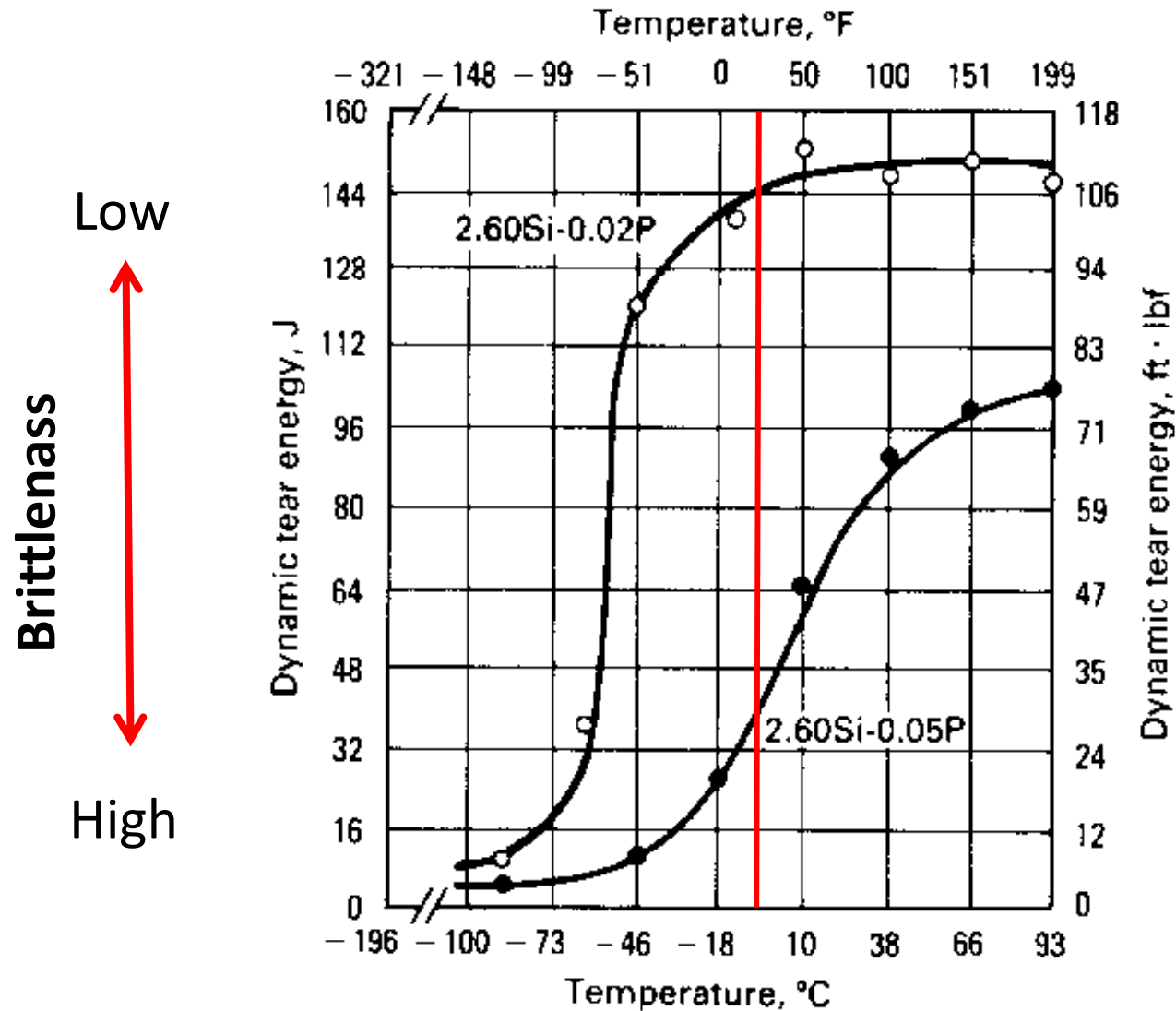
| Table The Composition of Steels from the <i>Titanic</i> , and ASTM A36 Steel | | | | | | | | | |
|--|------|------|-------|-------|-------|-------|-------|--------|------------|
| | C | Mn | P | S | Si | Cu | O | N | MnS: Ratio |
| <i>Titanic</i> Hull Plate | 0.21 | 0.47 | 0.045 | 0.069 | 0.017 | 0.024 | 0.013 | 0.0035 | 6.8:1 |
| ASTM A36 | 0.20 | 0.55 | 0.012 | 0.037 | 0.007 | 0.01 | 0.079 | 0.0032 | 14.9:1 |

The presence of relatively high amounts of phosphorous, oxygen, and sulfur has a tendency to embrittle the steel at low temperatures.

There is a high probability that the steel used in the *Titanic* was made in an acid-lined open-hearth furnace, which accounts for the fairly high phosphorus and high sulfur content.



Phosphorus and the Titanic



Effect of P on brittleness factor

That's why phosphorus should be removed from steel

Topedo-car (→)
transporter of 300 ton of hot metal
(molten pig iron) produced by BF to
BOF shop

Slag generated on the surface of
hot metal (↓)
Generally $\text{CaO-FeO-SiO}_2\text{-P}_2\text{O}_5$
P content :1~5



CaO and Fe_2O_3 (or O_2) are injected into hot metal
to oxidize phosphorus in iron and formed P_2O_5 is
stabilized in slag as calcium-phosphate

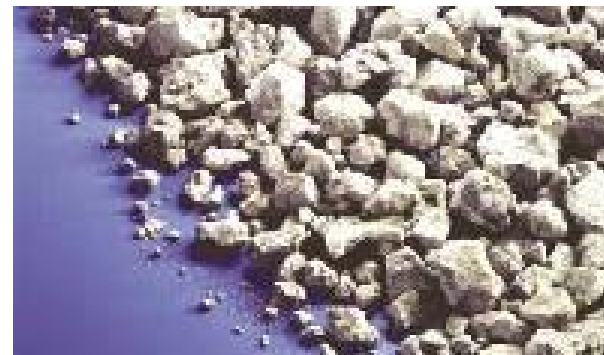
Tragedy of phosphorus in slag

“We are producing high quality steels, not slag”, steelmaker said.



Tragedy of phosphorus in slag

Slag is well recycled as road construction materials.
“After all, slag is slag”, steelmaker said.



Recent topics on phosphorus

Science, Vol 283, Issue 5410, 2015, 26 March 1999
[DOI: 10.1126/science.283.5410.2015]

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[Next Article](#) ▶

A Potential Phosphate Crisis

Philip H. Abelson

Phosphate is a crucial component of DNA, RNA, ATP, and other biologically active compounds. Microbes, plants, and animals—including humans—cannot exist without it. Rocks containing phosphate have been discovered and are being mined at minimal cost. But resources are limited, and phosphate is being dissipated. Future generations ultimately will face problems in obtaining enough to exist.

The current major use of phosphate is in fertilizers. Growing crops remove it and other nutrients from the soil. Long-term research at the Morrow agricultural plots of the University of Illinois at Urbana-Champaign has corroborated the fact that even the best land loses fertility unless nutrients are replenished. At the Morrow plots, there is a threefold or greater difference in yields of corn between fertilized areas and untreated ones. Most of the world's farms do not have or do not receive adequate amounts of phosphate. Feeding the world's increasing population will accelerate the rate of depletion of phosphate reserves.

Recent topics on phosphorus


Technology Solutions

Closing the phosphorus loop

Sources of high-grade phosphate ore deposits could disappear within the next 100 years at current use rates, analysts say. In the hunt for alternatives to mining this nonrenewable, unique resource, researchers have found one possible surprising new source: sewage treatment plants.

About 90% of the phosphate dug out of the ground goes into fertilizer; the remainder is used in products including food additives, glues, flame retardants, and detergents, according to Chris Thornton of the Centre Européen d'Etudes des Polyphosphates (CEEP), the phosphate industry research association housed at the European Chemical Industry Council. "If it runs out, then there's no more agriculture as we know it," Thornton points out. "The amount that can be reasonably recycled from sewage is

calcium silicate hydrates (CSHs), which are byproducts of the building material industry, to remove phosphorus through crystallization. It's a simple, one-step process that removes phosphorus directly from the wastewater stream and recovers it without the addition of




FLORIDA ANALOGUE OF PHOSPHATE RESOURCES

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Env. Sci. Tech., (2007), pp.2078.

RECYCL-1907; No. of Pages 21 **ARTICLE IN PRESS**

Available online at www.sciencedirect.com



ScienceDirect

Resources, Conservation and Recycling xxx (2006) xxx–xxx

www.elsevier.com/locate/resconrec

**Resources
Conservation &
Recycling**

Comparative analysis of phosphorus use within national and local economies in China

Yi Liu^{a,*}, Jining Chen^a, Arthur P.J. Mol^b, Robert U. Ayres^{c,d}

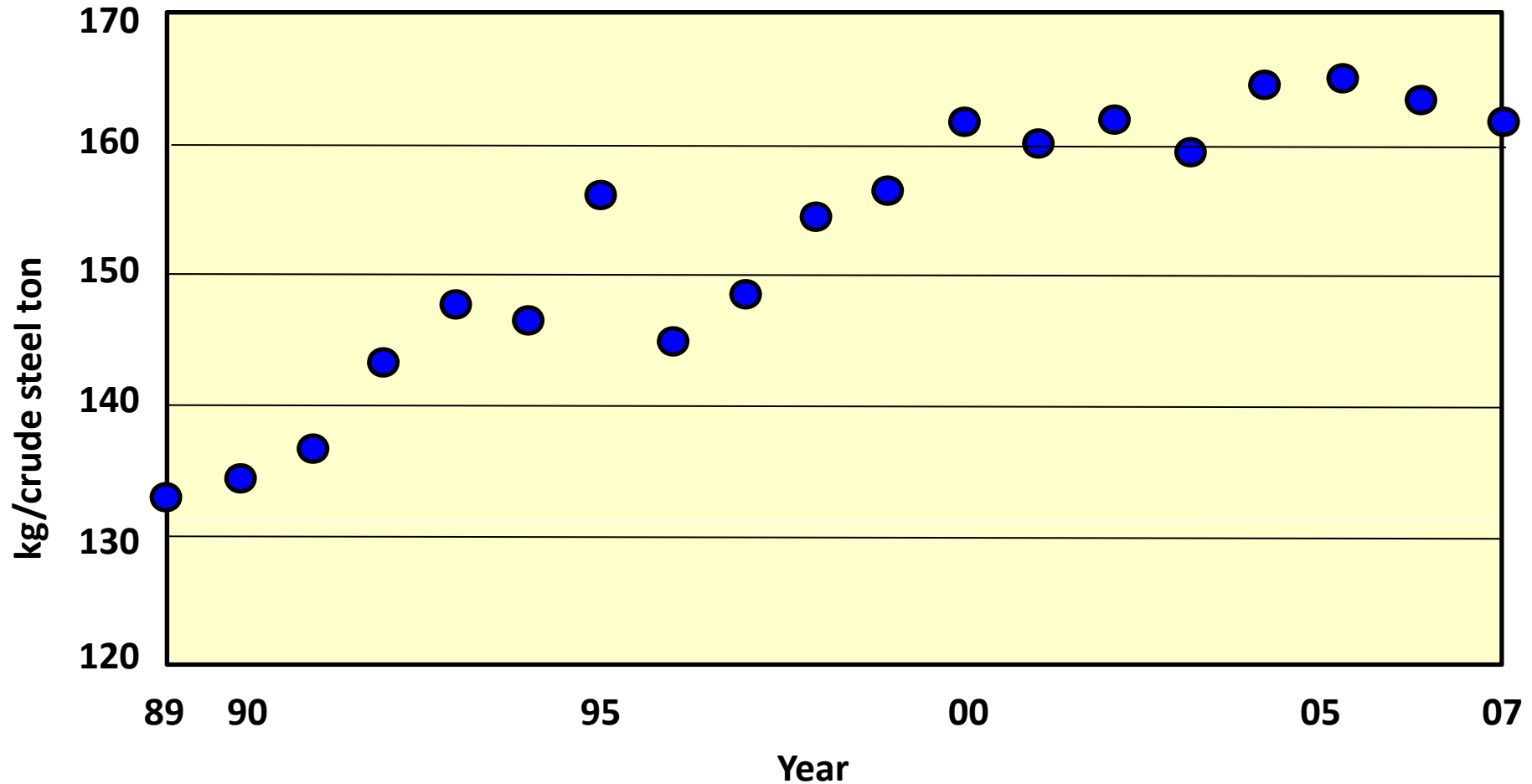
Annu. Rev. Energy Environ. 2000. 25:53–88
Copyright © 2000 by Annual Reviews. All rights reserved

PHOSPHORUS IN THE ENVIRONMENT: Natural Flows and Human Interferences

Vaclav Smil
Department of Geography, University of Manitoba, Winnipeg, Manitoba R3T 2N2
Canada; e-mail: vsmil@cc.umanitoba.ca

Phosphorus in the Global Environment. Transfers, Cycles and Management. H. Tiessen (Editor). Wiley, Chichester, 1995. Hardcover x11 + 462 pp. ISBN 0-471-95691-0.

Trend of steelmaking slag generation in Japan

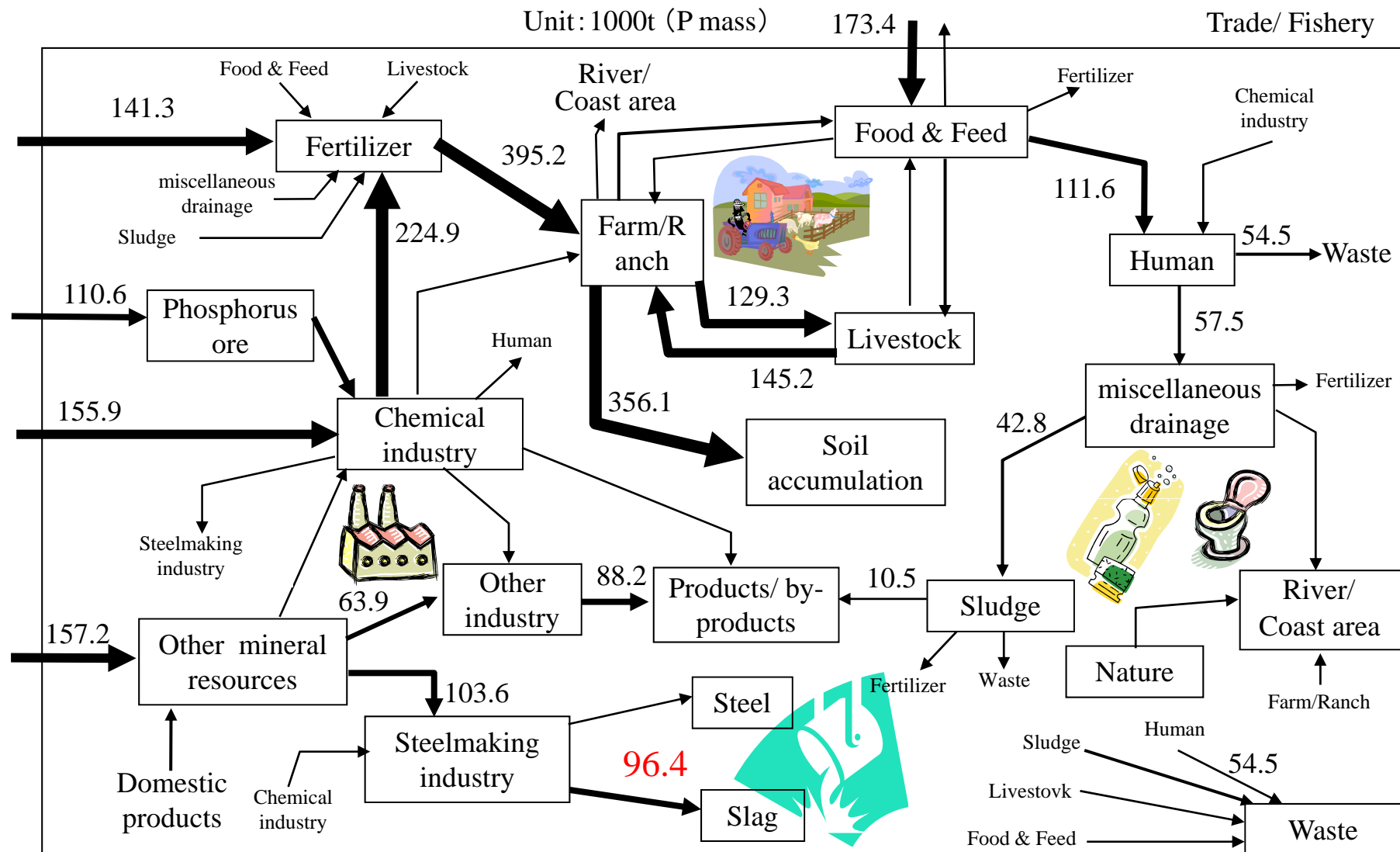


(120 million ton of crude steel) x 160 kg/crude steel t = 19 million ton of slag

In short...

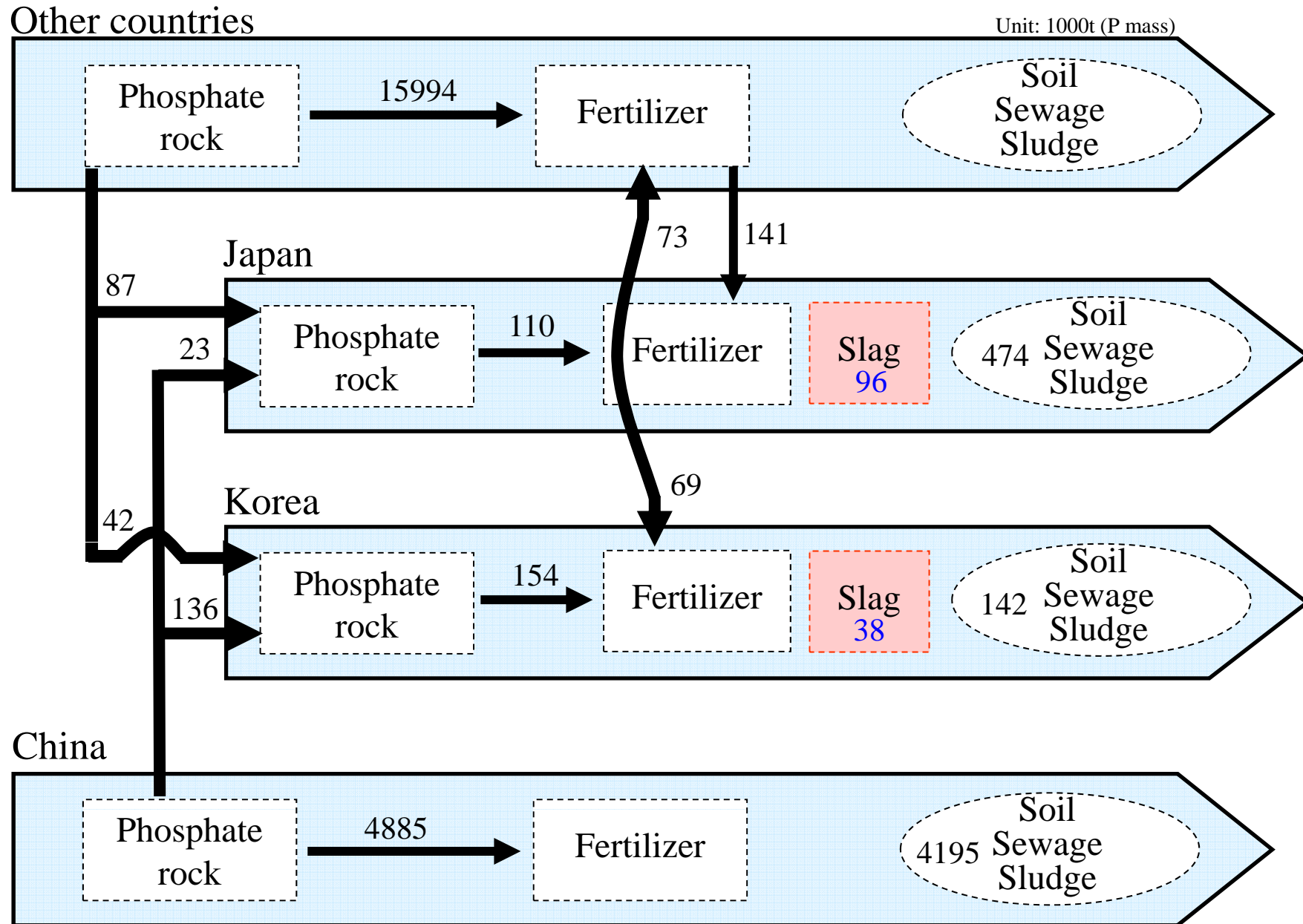
- Phosphorus is very important and strategic resource for us while it is a kind of a natural enemy for steelmaker.
- We don't know exactly how much phosphorus goes through our society.
- On the other hand....., the amount of phosphorus which goes through steelmaking industry should be very large.

Domestic material flow of phosphorus

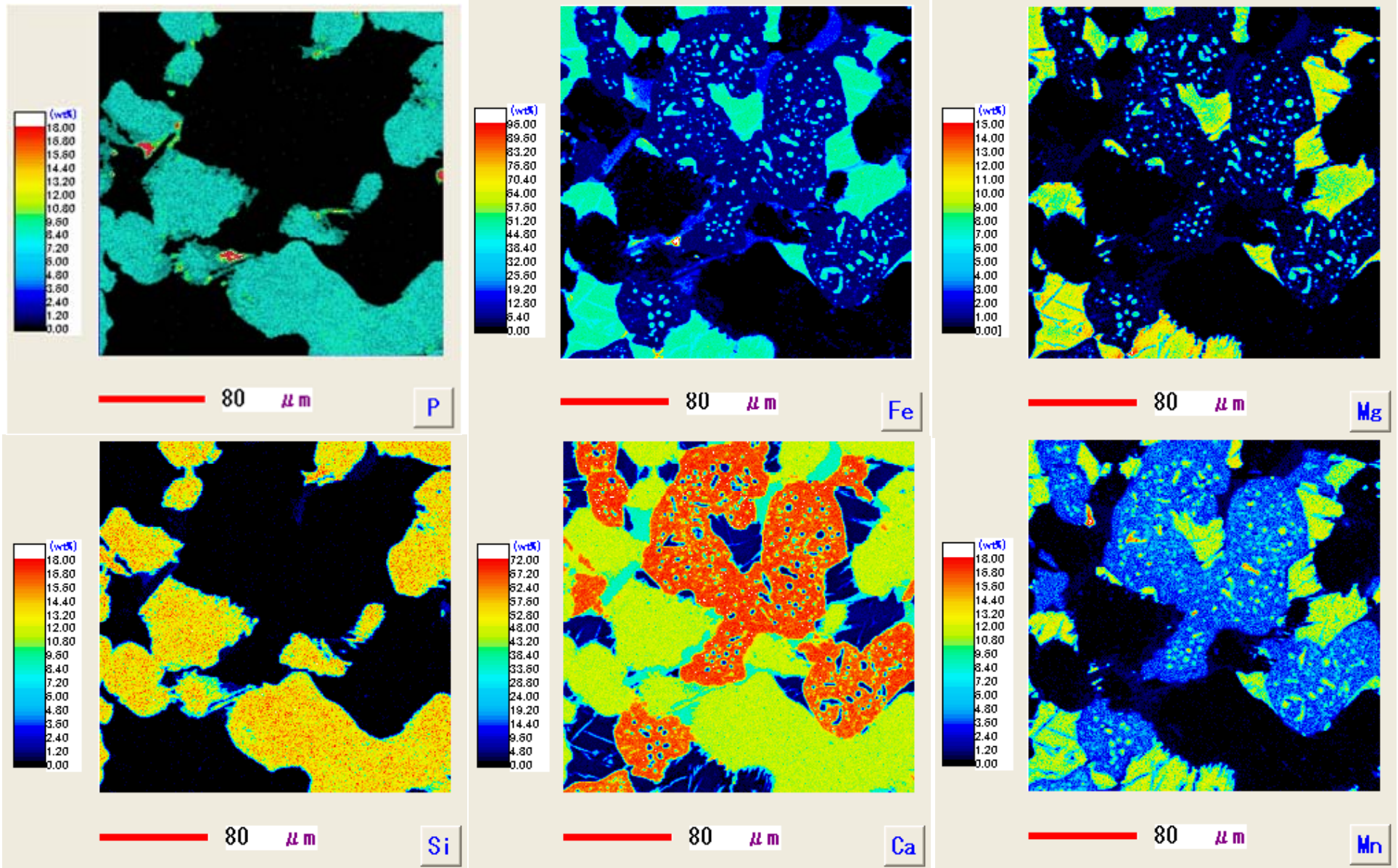


Material flow of P among countries

Y.-S. Jeong, H. Kubo, K. Matsubae-Yokoyama, J.-J. Pak and T. Nagasaka: Substance Flow Analysis of Phosphorus and Manganese Correlated with Korean Steel Industry, Resources, Conservation and Recycling, **53** (2009), 479-489

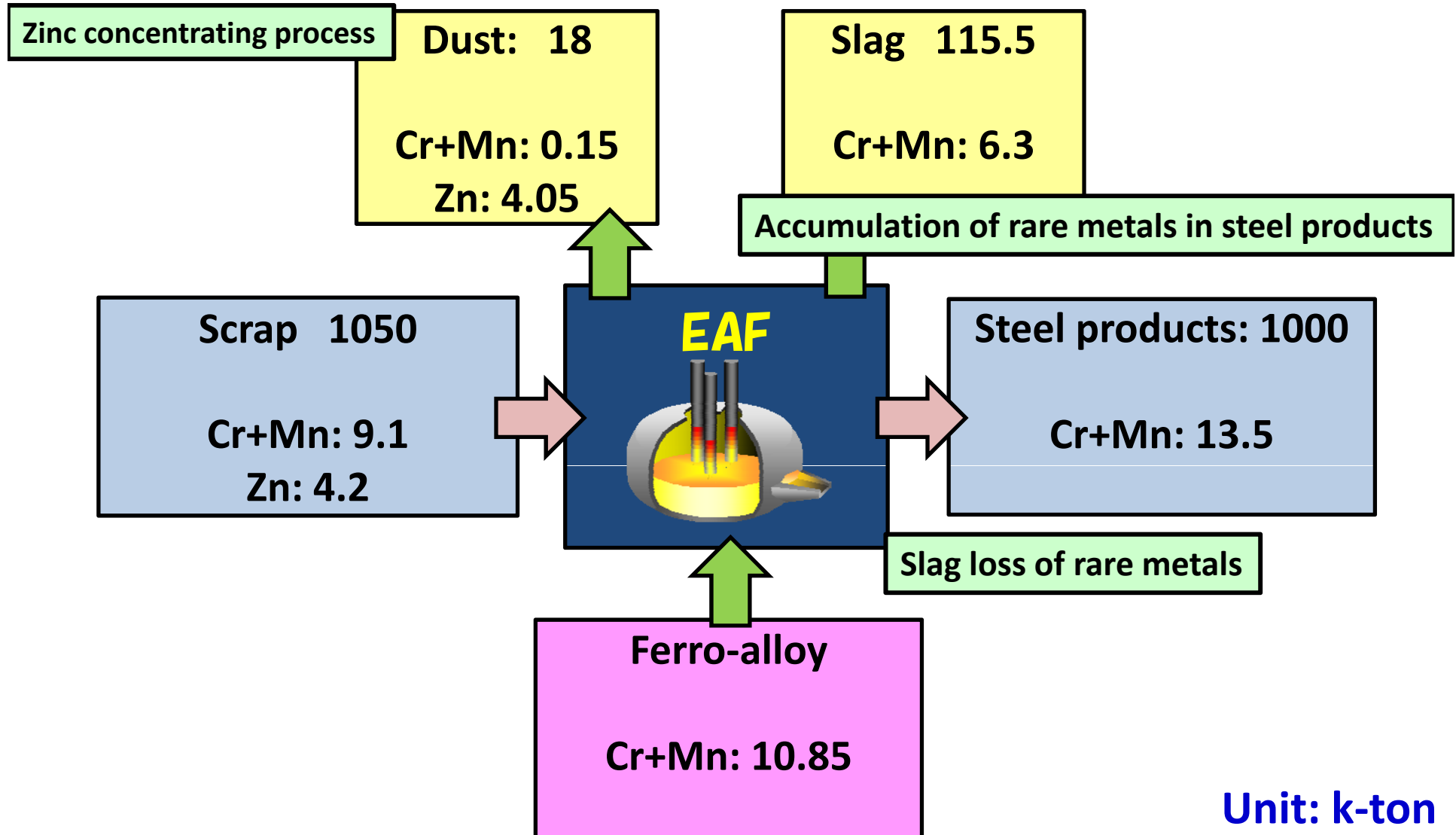


Micro-structure of slag after cooling




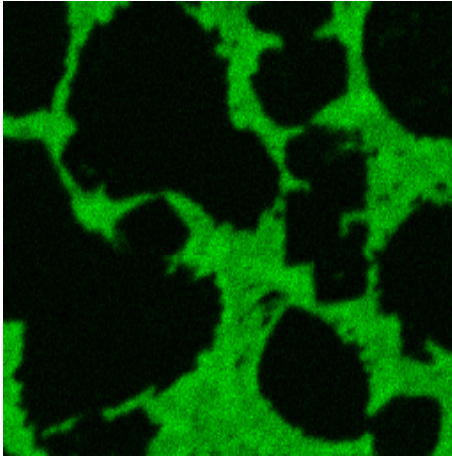
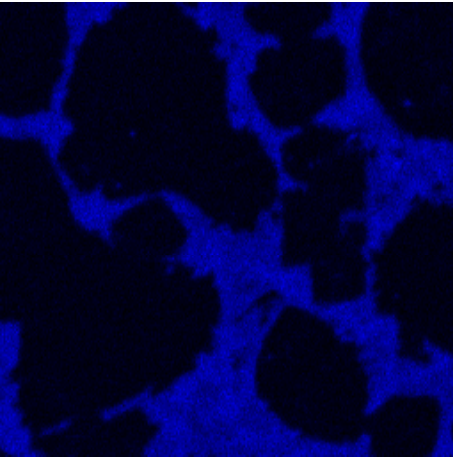
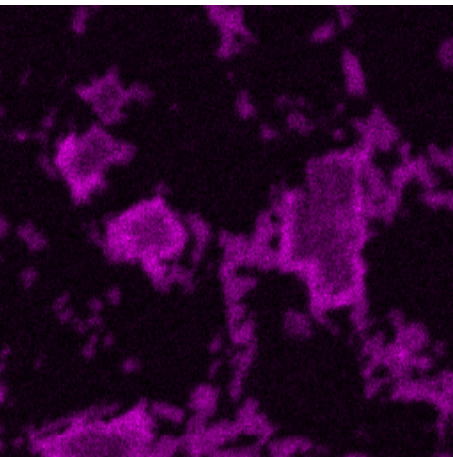
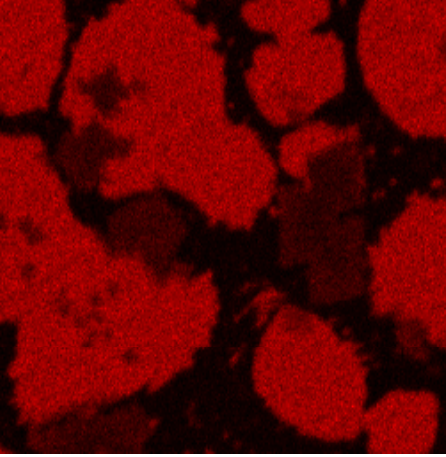
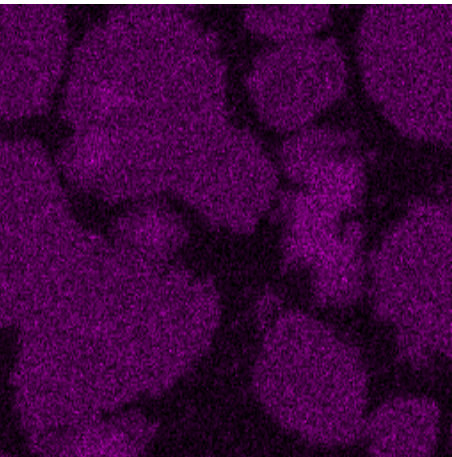
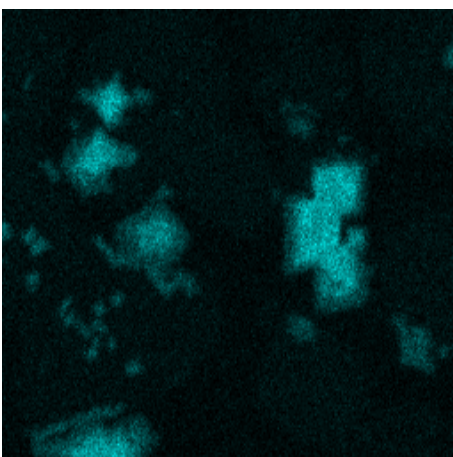
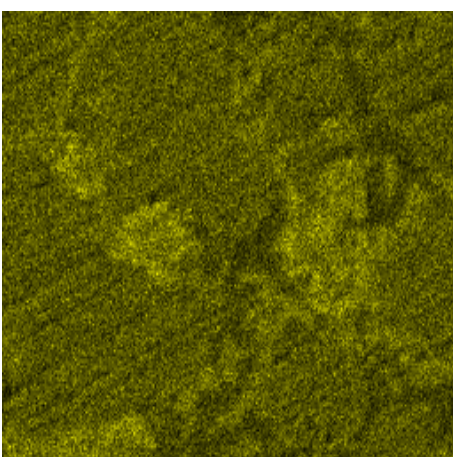
Rare metals (Cr+Mn+Zn) balance in EAF process

Average of three steel works which produce about 1000 k-ton/year



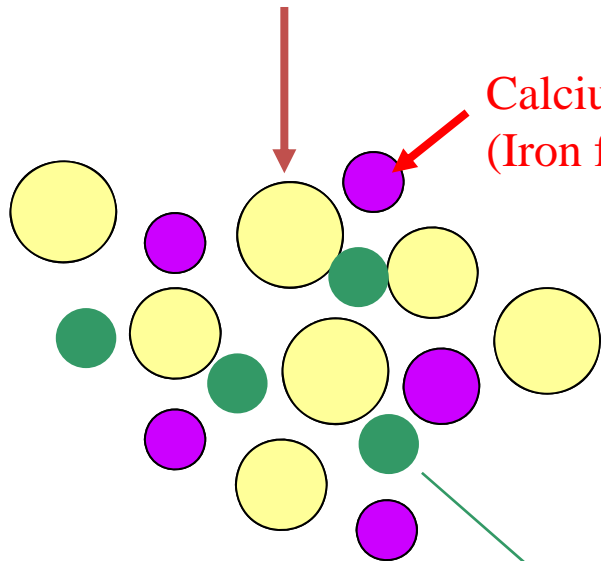
Micro-structure of slag for special bar steel

— 100 μm

| Image | Ca | Si | Al |
|--|---|--|--|
|  <p>1,000x 10.0 μm WD:20.2mm 20kV 2003/07/23 14:05:24 8</p> |  |  |  |
| Fe | Mn | Cr | Mg |
|  |  |  |  |

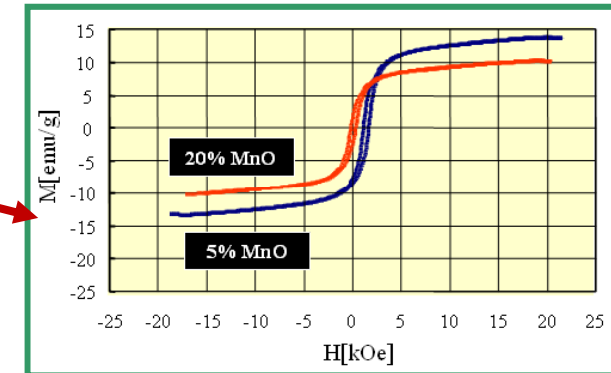
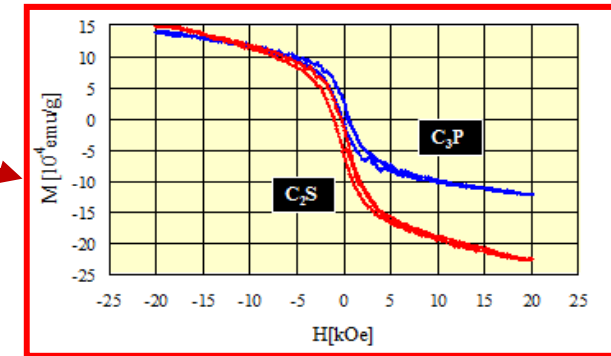
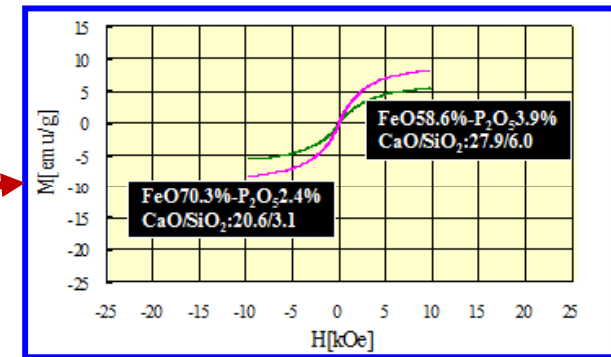
Possibility of magnetic separation

Matrix phase FeO-CaO-SiO₂(MnO)



Calcium phosphate
(Iron free)

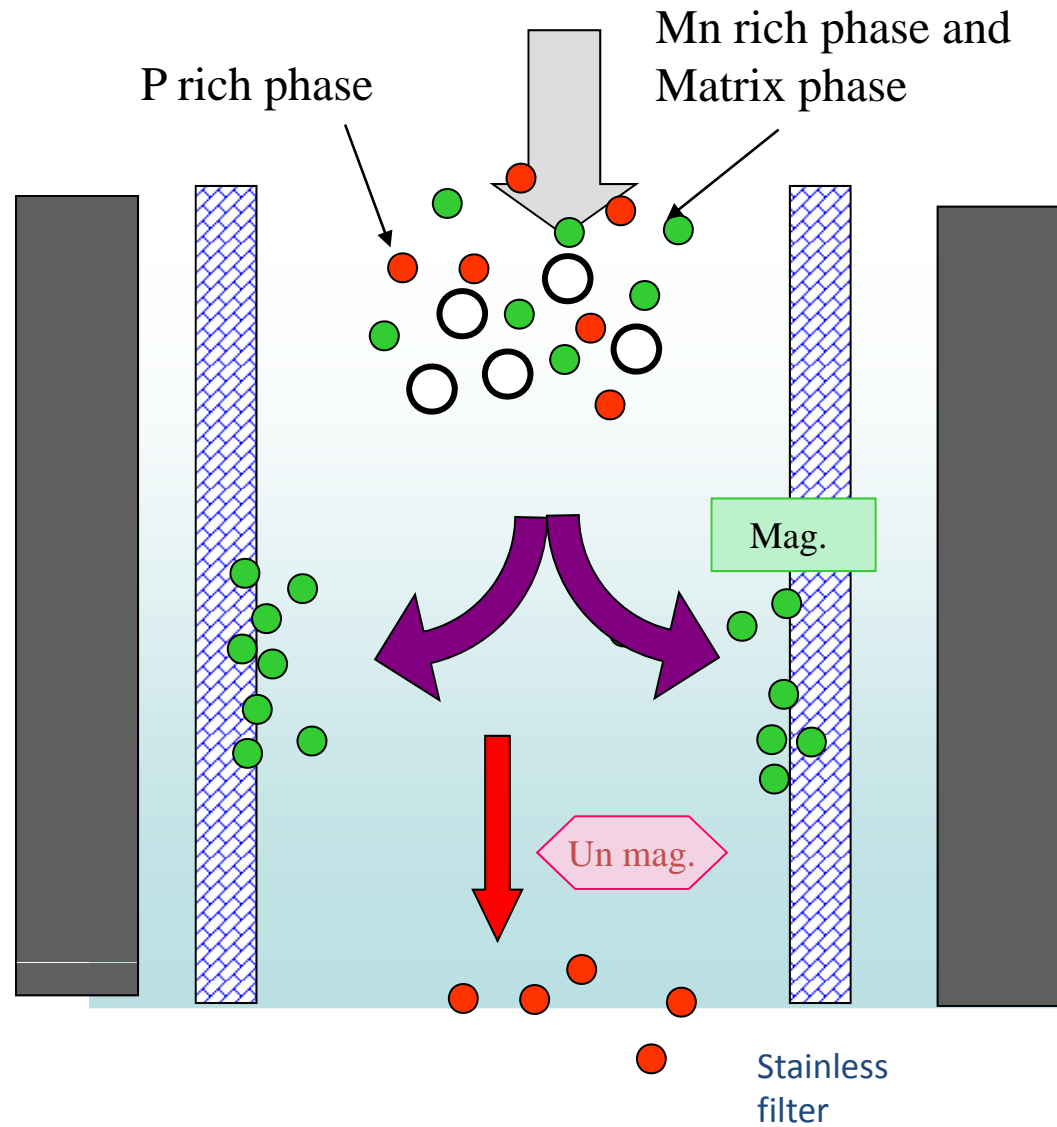
MnO-FeO



Trial of magnetic separation

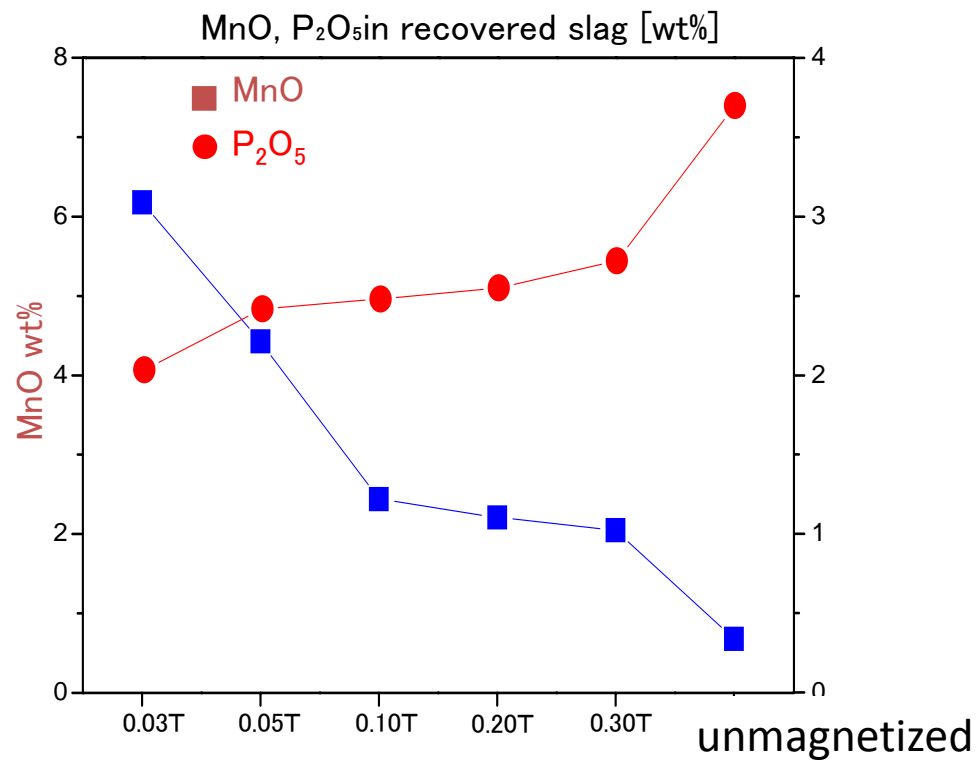
< Wet High Intensity Separators >

- Eriez Series L Model 4 Laboratory -

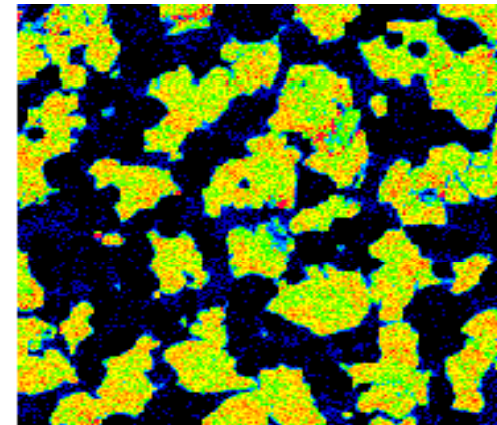


results

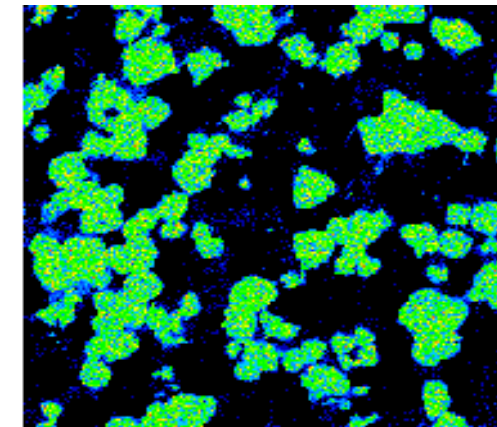
| FeO | CaO | SiO ₂ | P ₂ O ₅ | MnO |
|-------|-------|------------------|-------------------------------|------|
| 22.51 | 42.36 | 11.05 | 2.24 | 3.49 |



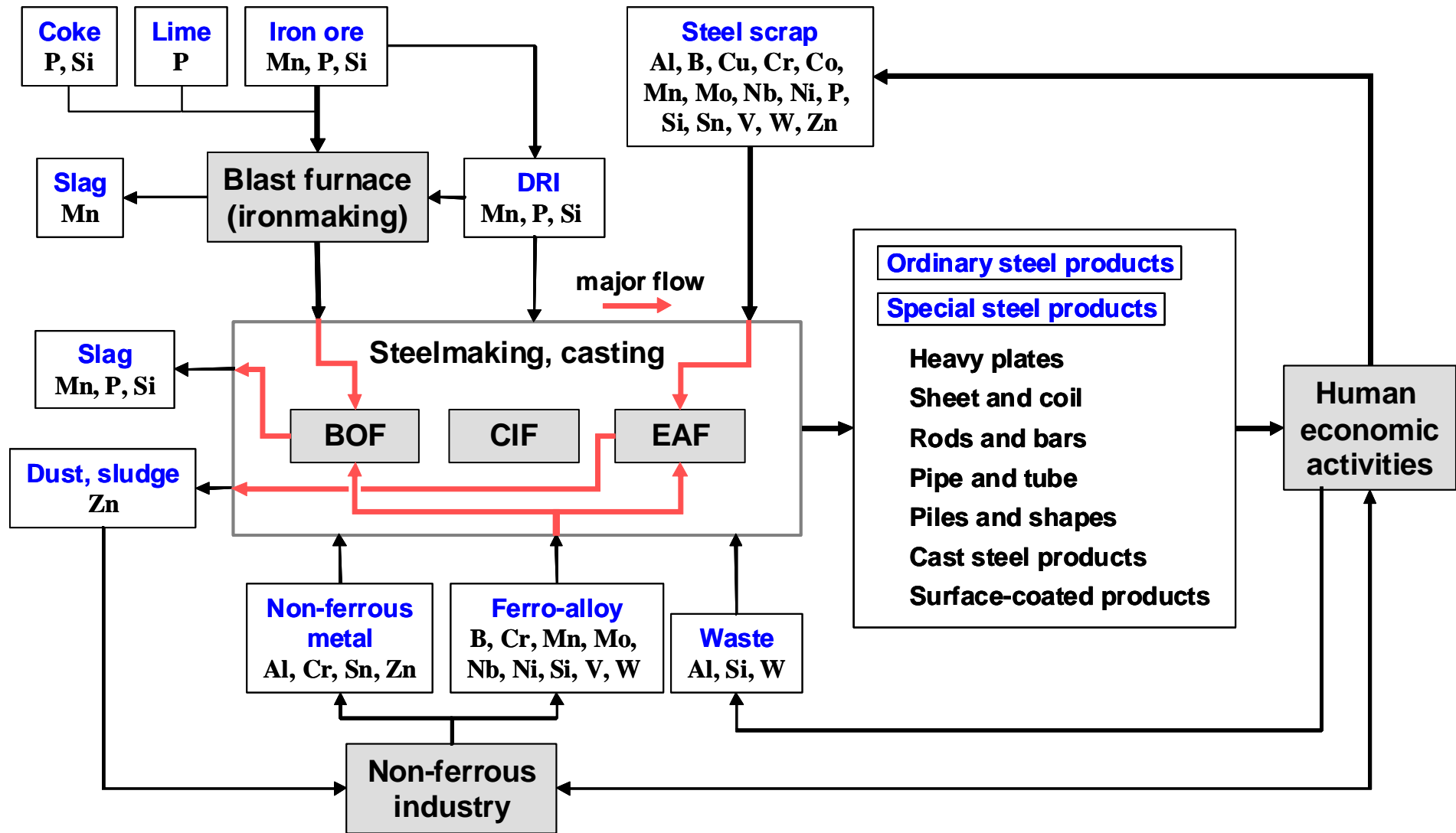
P



Mn



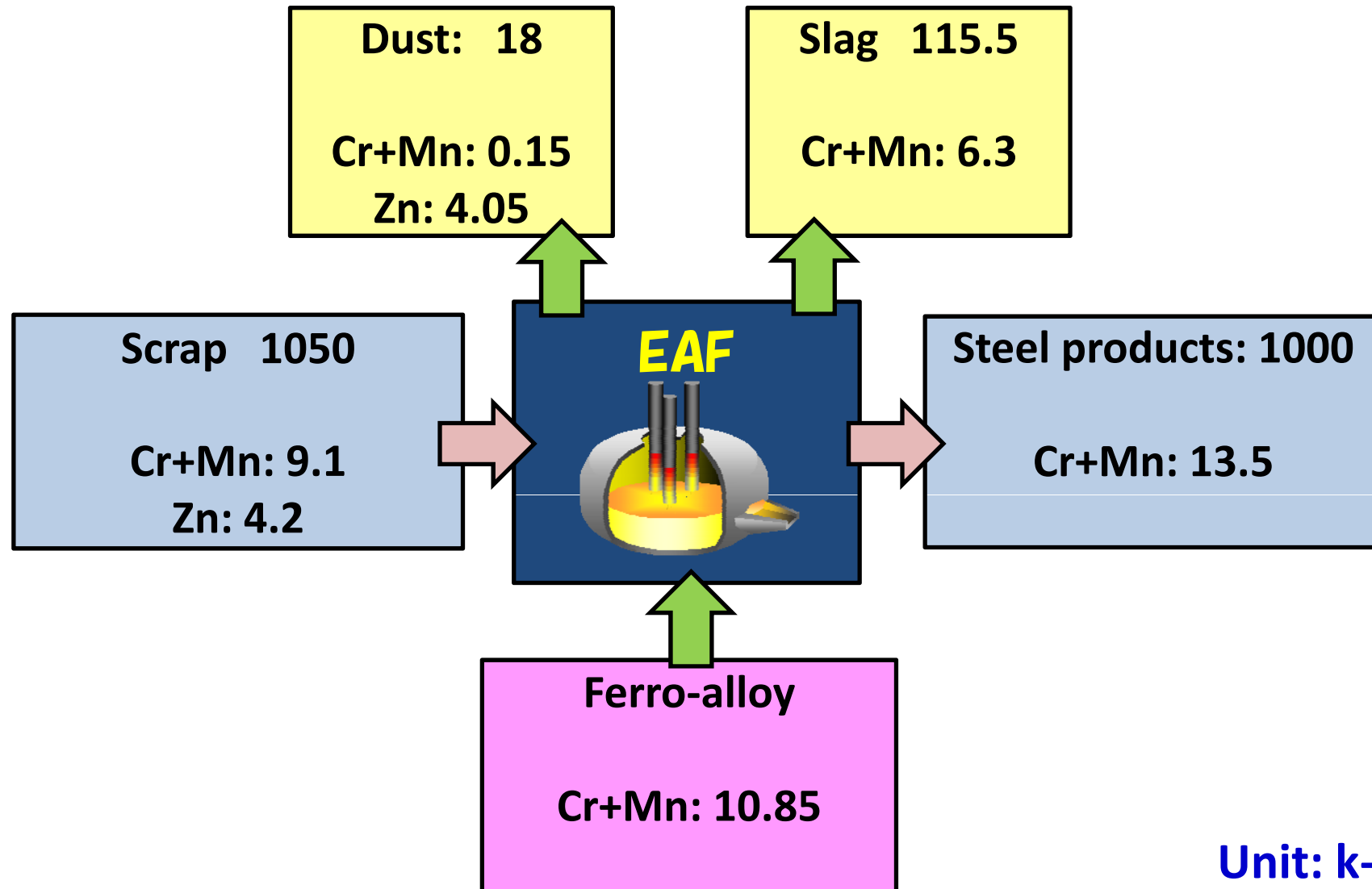
What about "dust-making technology" ?



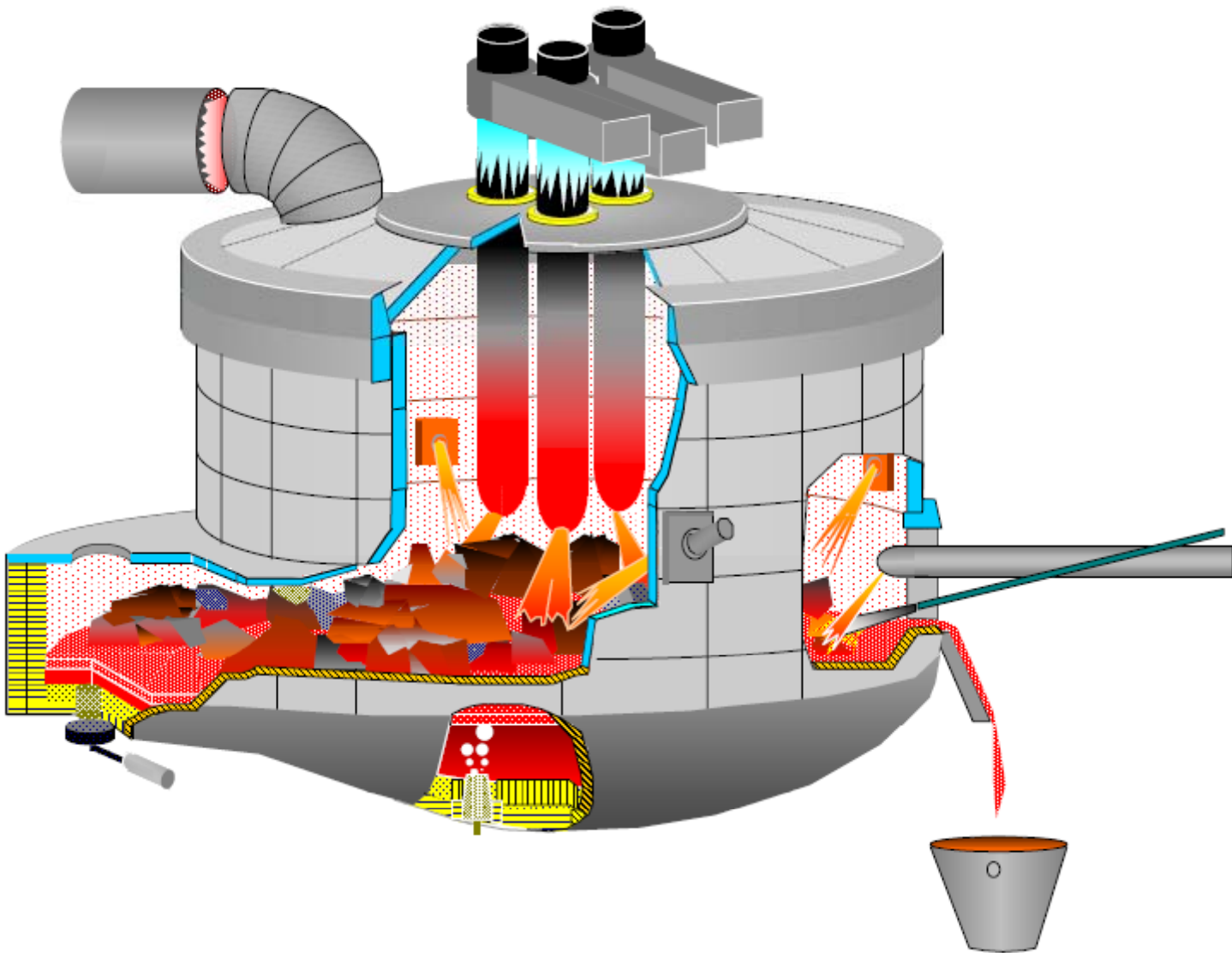
Rare metals in the life-cycle of steel products

Rare metals (Cr+Mn+Zn) balance in EAF process

Average of three steel works which produce about 1000 k-ton/year



EAF process

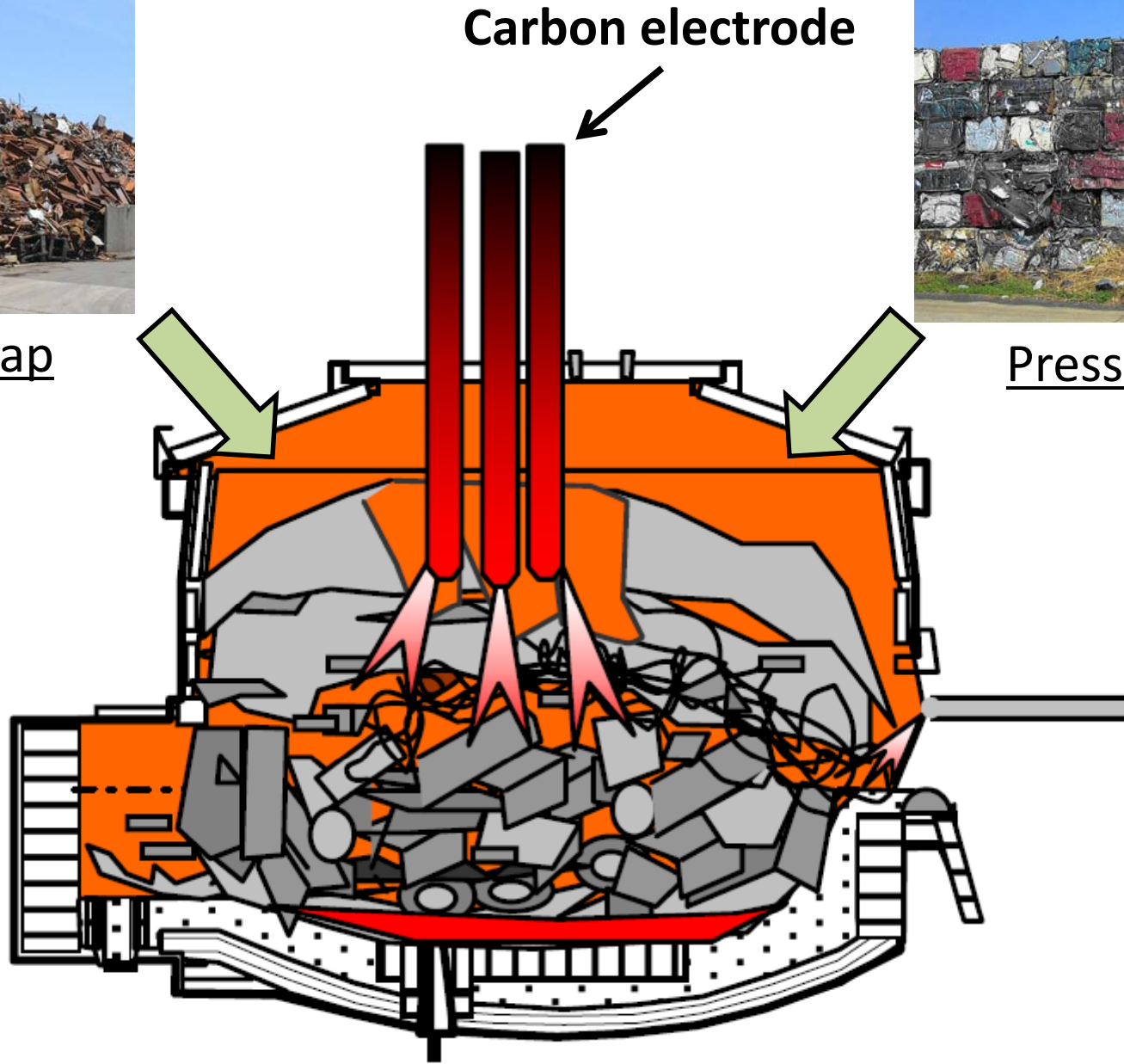




Heavy scrap



Pressed scrap

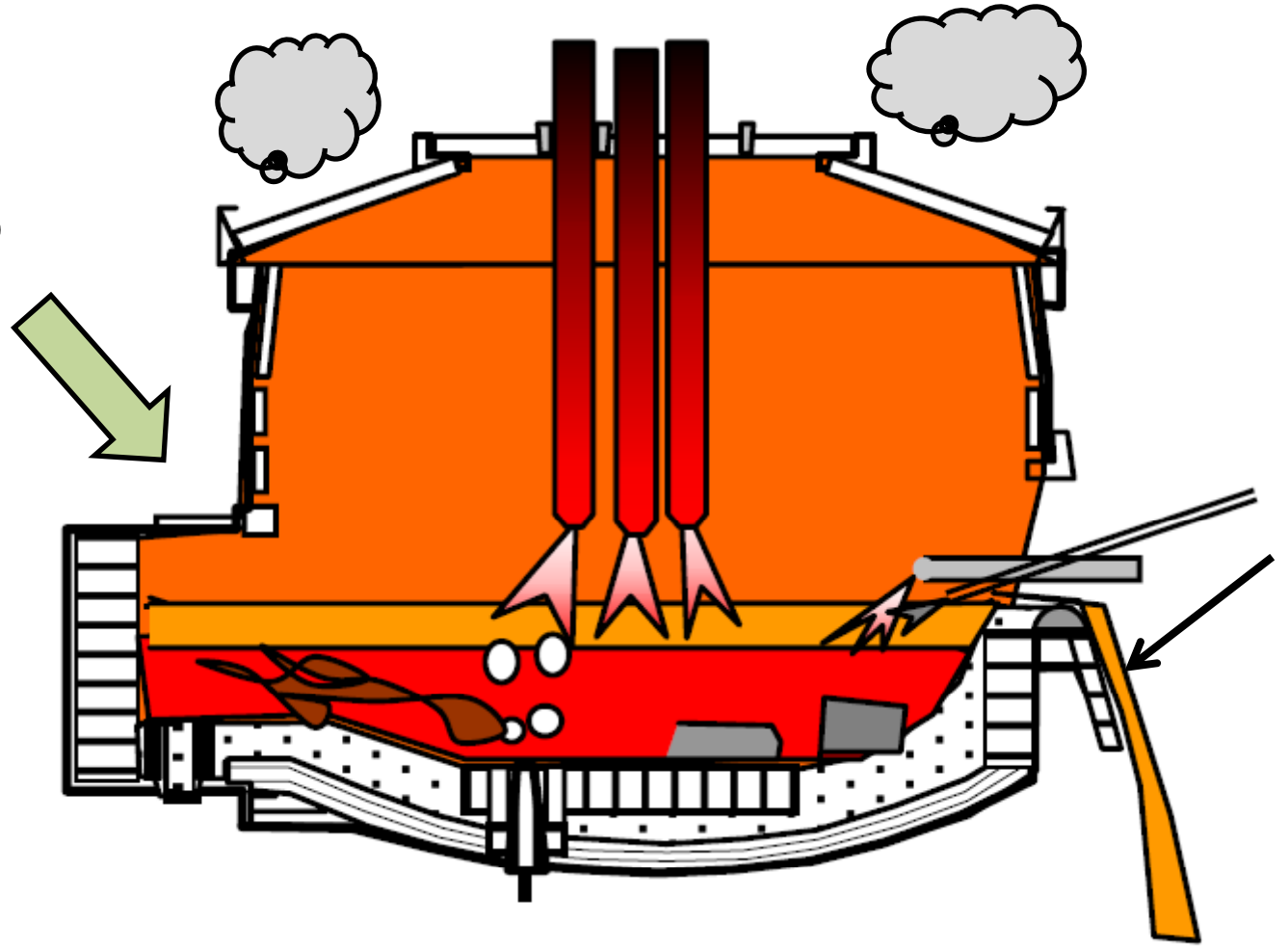
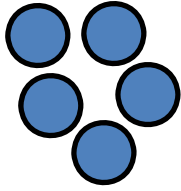


dust

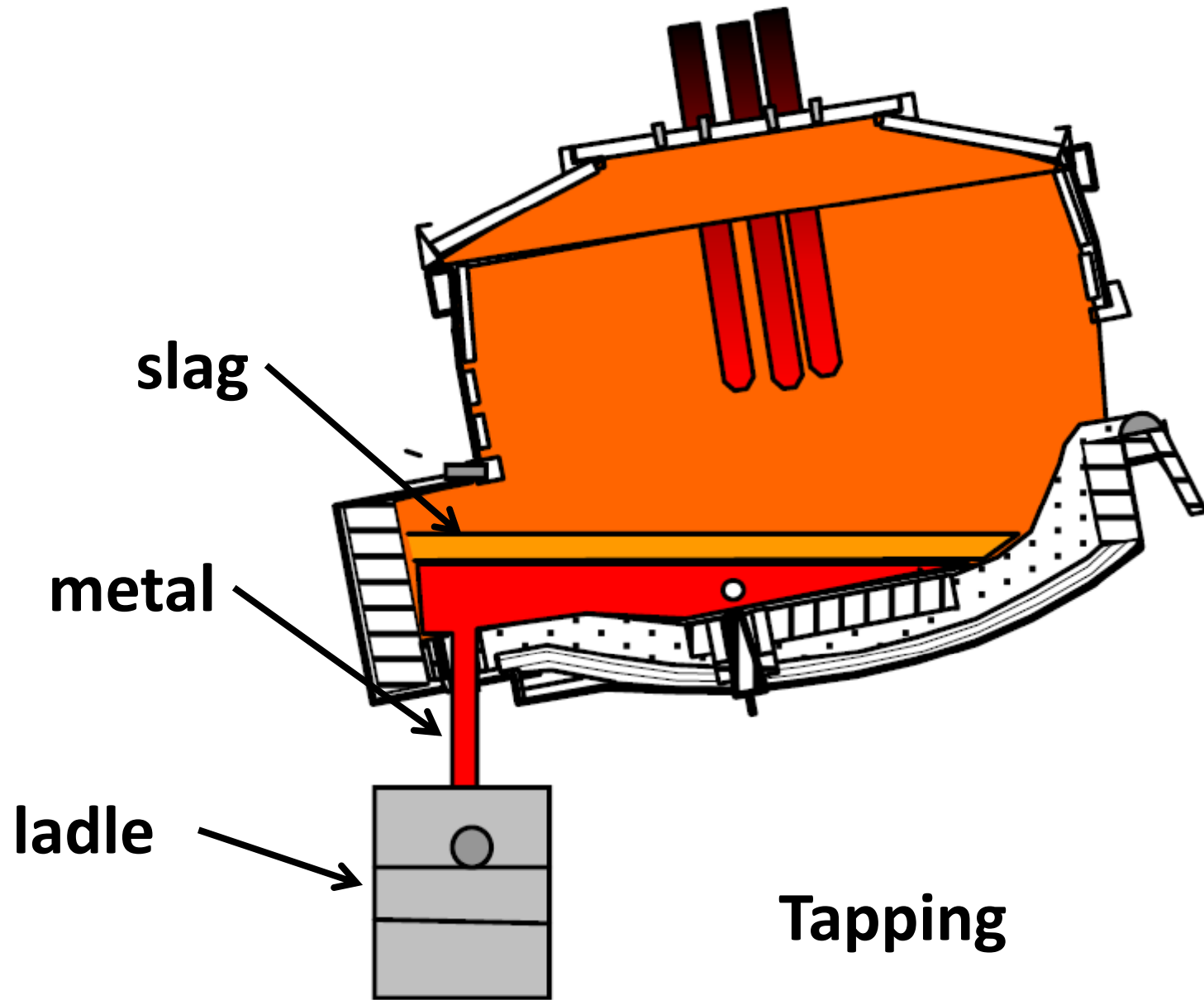


EAF Dust: Zn 20-30%, Fe 25-35%, Cl+F 5-15%, Pb, Cd, etc.

ferro-
alloys

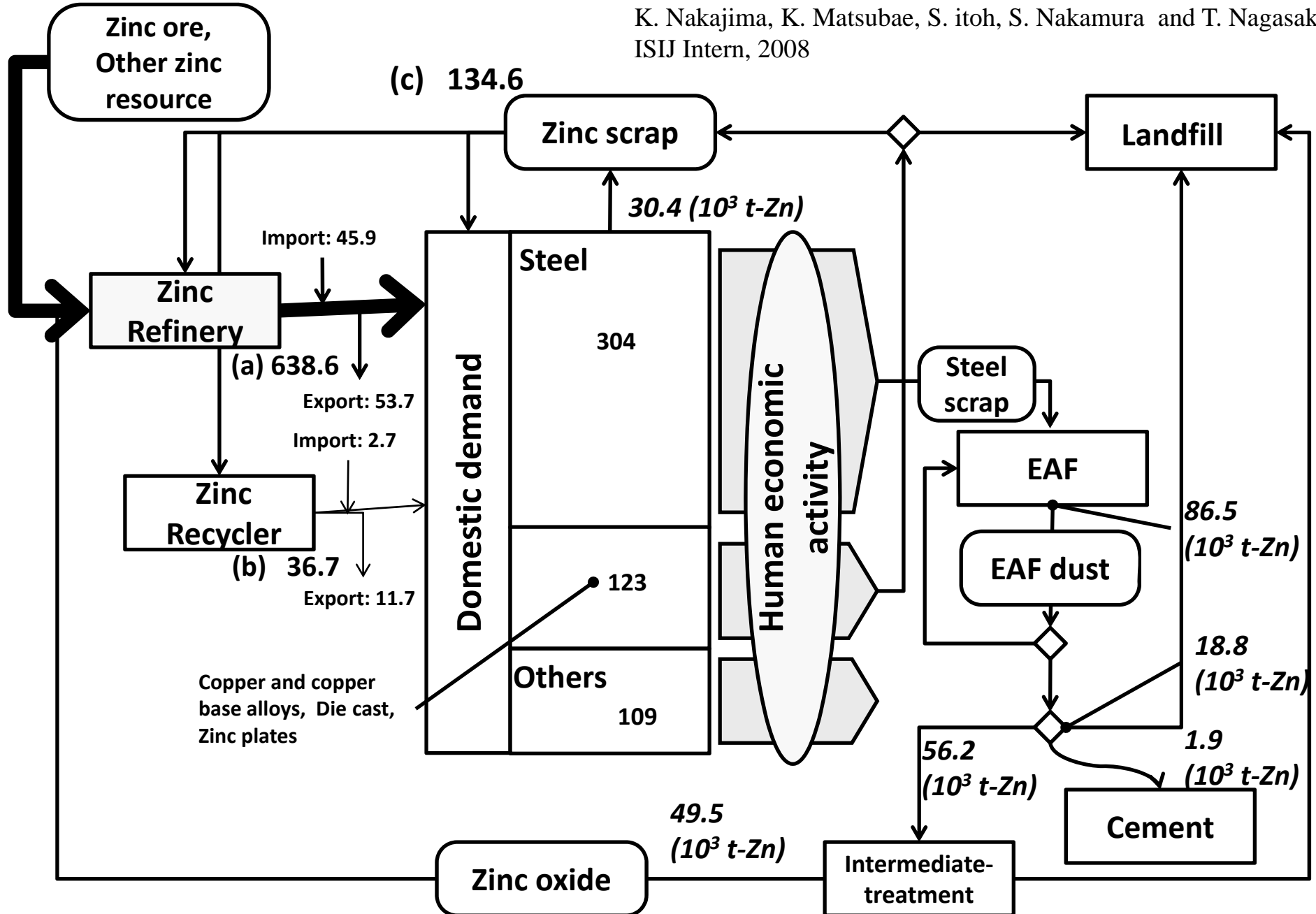


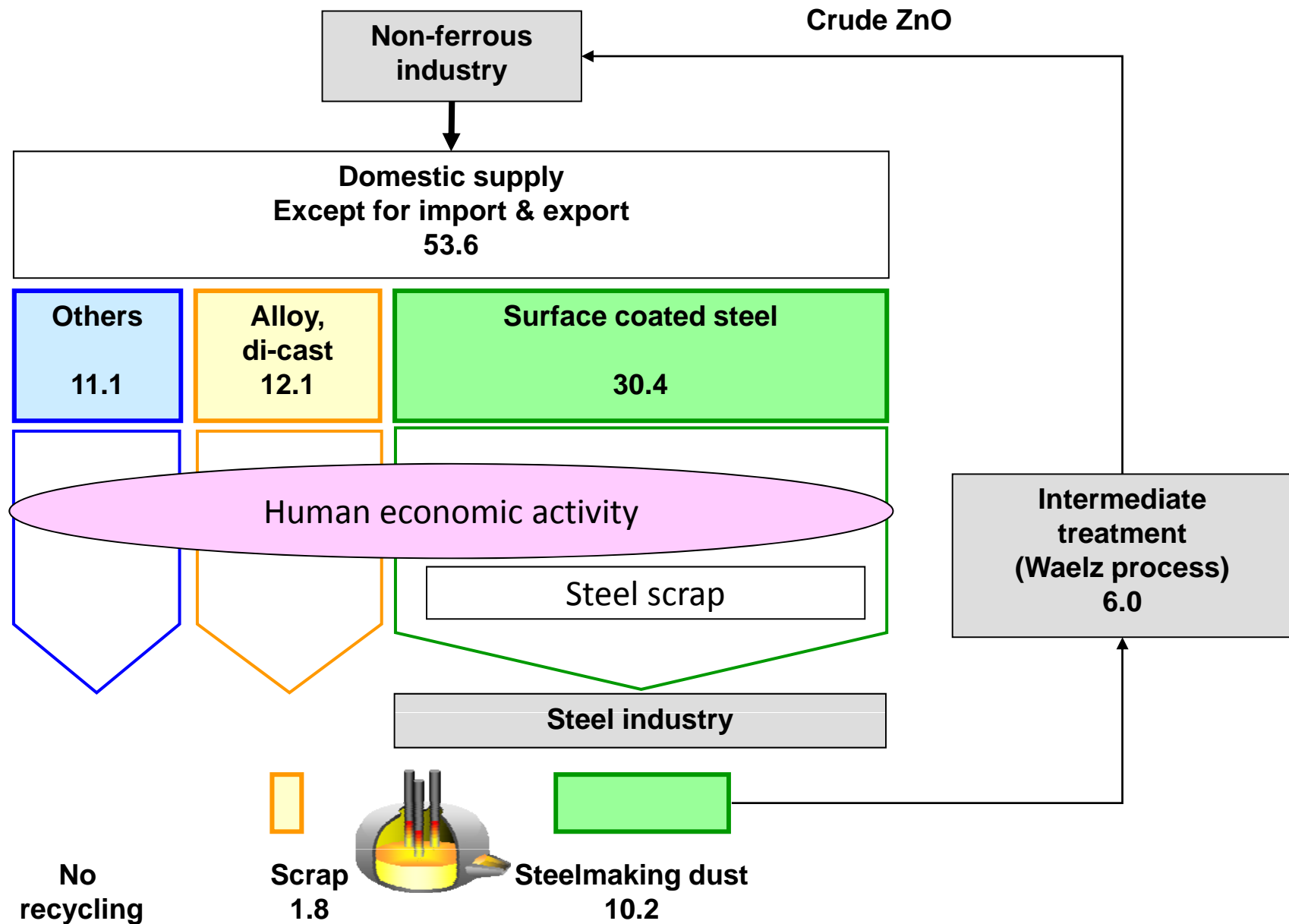
slag



Zinc flow in Japan

K. Nakajima, K. Matsubae, S. Itoh, S. Nakamura and T. Nagasaka:
 ISIJ Intern, 2008





Conclusion

EAF acts extremely important role for sustainable steel cycle and rare metals consumption.

Understanding and control of substance flow through the life-cycle of steel products are also very important.

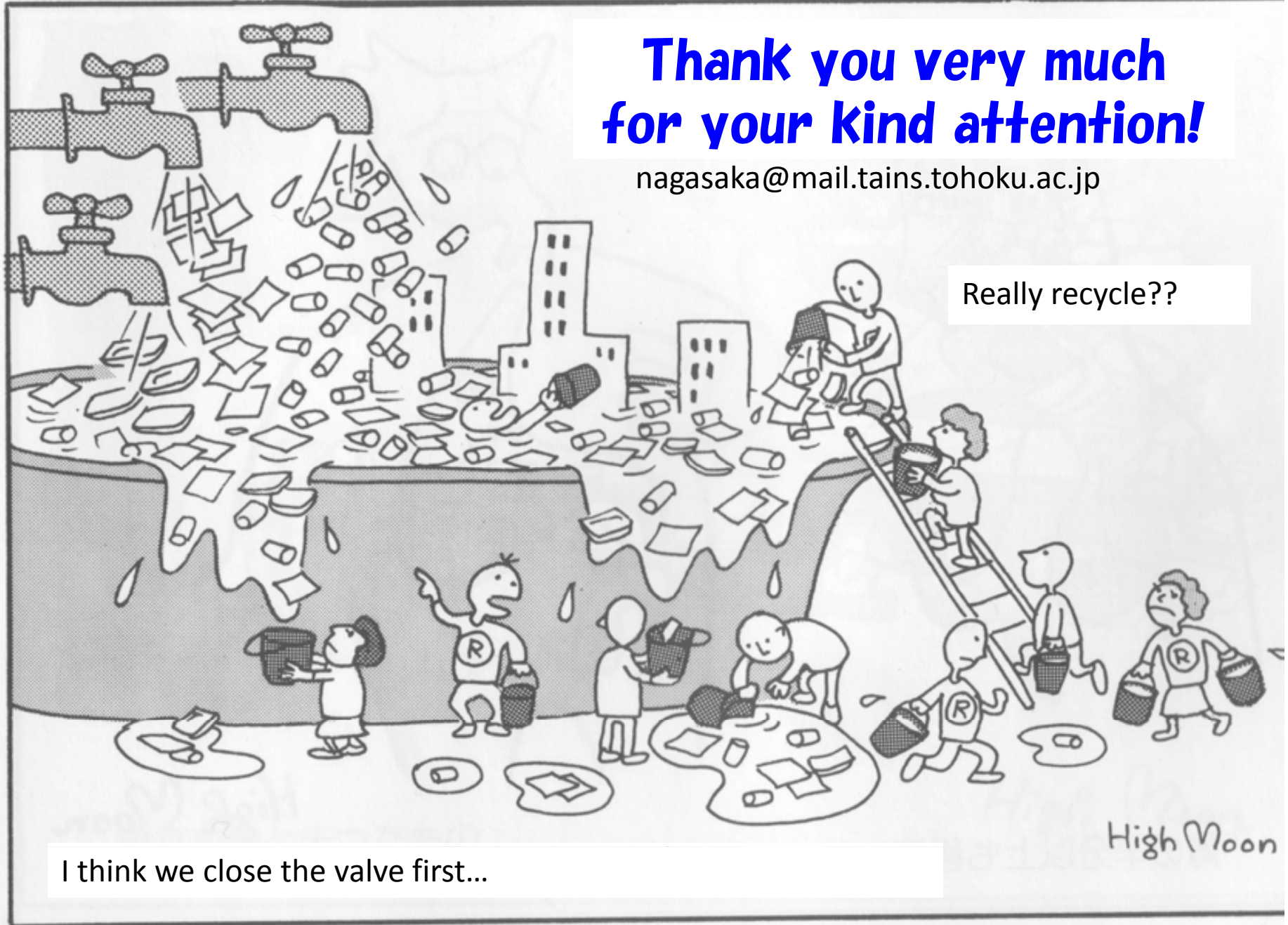
Scrap sorting based on the composition and slag-making technology will result in great saving of rare metal consumption in steel-making.

It may be possible to co-product high quality steel and zinc in EAF process.

**Thank you very much
for your kind attention!**

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Really recycle??



I think we close the valve first...

High Moon

