INSTITUTO DE PESQUISAS TECNOLÓGICAS

COMUNICAÇÃO TÉCNICA

Nº 174103

Project: Nd/Di production from CBMM Didymium oxide

João Batista Ferreira Neto.

Palestra apresentada no Workshop Brasil-Alemanha em Terras Raras no IPT, São Paulo, 2016

Instituto de Pesquisas Tecnológicas do Estado de São Paulo S/A - IPT
Av. Prof. Almeida Prado, 532 | Cidade Universitária ou
Caixa Postal 0141 | CEP 01064-970
São Paulo | SP | Brasil | CEP 05508-901
Tel 11 3767 4374/4000 | Fax 11 3767-4099

www.ipt.br

Summary

- IPT and Center for Technology in Metallurgy and Materials

  - Laboratory of Metallurgical Processes

    - Examples of R&D&I projects

- Project: Didymium production from CBMM oxide

  Next step….. Alloy and magnet production

- Possibilities of Cooperation with German Institutions and Universities

INSTITUTO DE PESQUISAS TECNOLÓGICAS

Institute for Technological Research

Technological solutions

Who we are

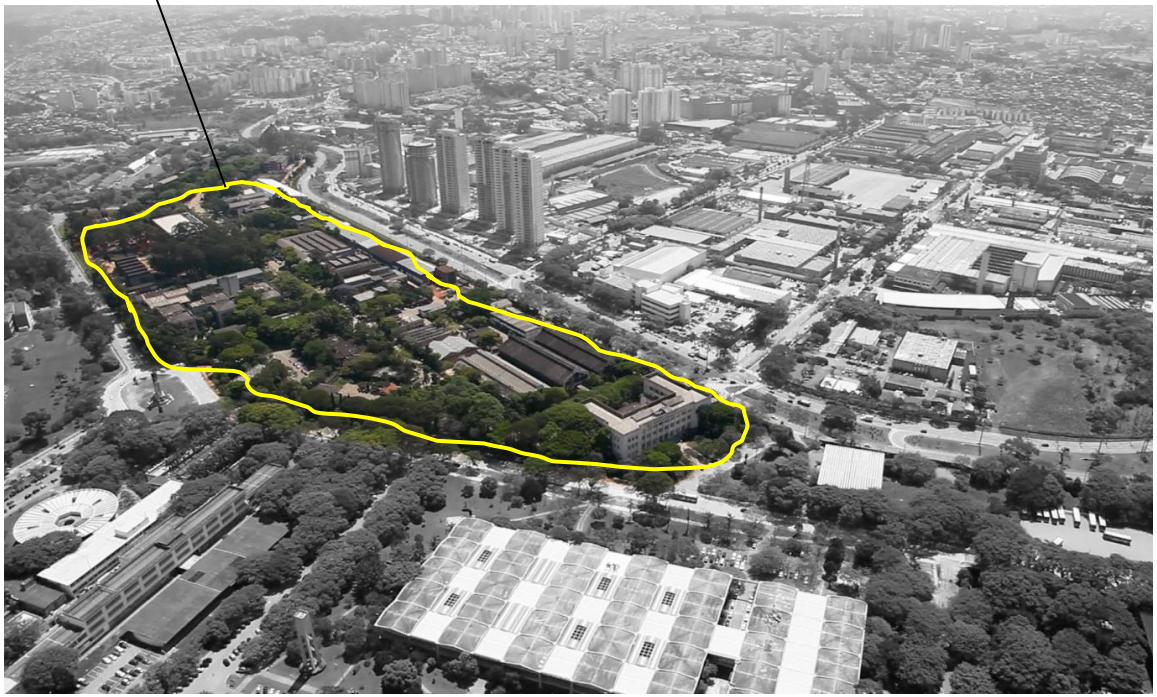
- Institute for Technological Research of the State of São Paulo S.A.
- One of the first applied R&D&I institutions in Brazil and the largest applied multipurpose R&D&I institution in Latin America
- Belongs to the Development Secretariat of the State of São Paulo
- IPT provides technological solutions to public and private companies and institutions

ipt

Where we are

Units

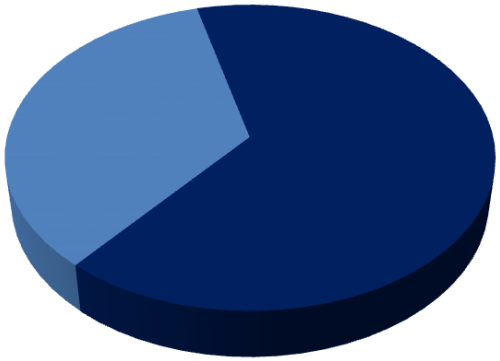
- São Paulo
- São José dos Campos (composite materials)
- Franca (individual protection equipment)



2015 Figures

- Annual revenue: **US$ 45 million**

35 % State of São Paulo Government



65 % R&D contracts and services

Human Resources Dec. 2015	
Researchers	381
Technicians	196
Administrative Support	250
Interns	80
Total	907

Technical Production:

- Technical Documents: **22,661** technical reports
- Number of clients: **3,794**
- Ongoing projects: **145**
- Publications: **302** papers in journals and congresses
- Patents and softwares: **10**

1.00 USD = 3,9042 BRL

ipt INSTITUTO DE PESQUISAS TECNOLÓGICAS

Technical Activities 2015

Innovation, research and development

31% of the total revenue

(TARGET : 40% IN 2018)

Technological Services

26,6% of the total revenue

Development and metrological support

41,9% of the total revenue

Information and technology education

0,5% of the total revenue

ipt INSTITUTO DE PESQUISAS TECNOLÓGICAS

Markets

Energy

- Oil and gas
- Ethanol

Transportation

- Roads
- Naval
- Pipeline
- Metro-railway
- Airspace
- Cargo
- IT & ITS

Materials and Chemistry

- Metallurgy
- Chemistry
- Bioproducts
- Plastics & Rubber
- Composites
- Textiles & Leather
- Wood

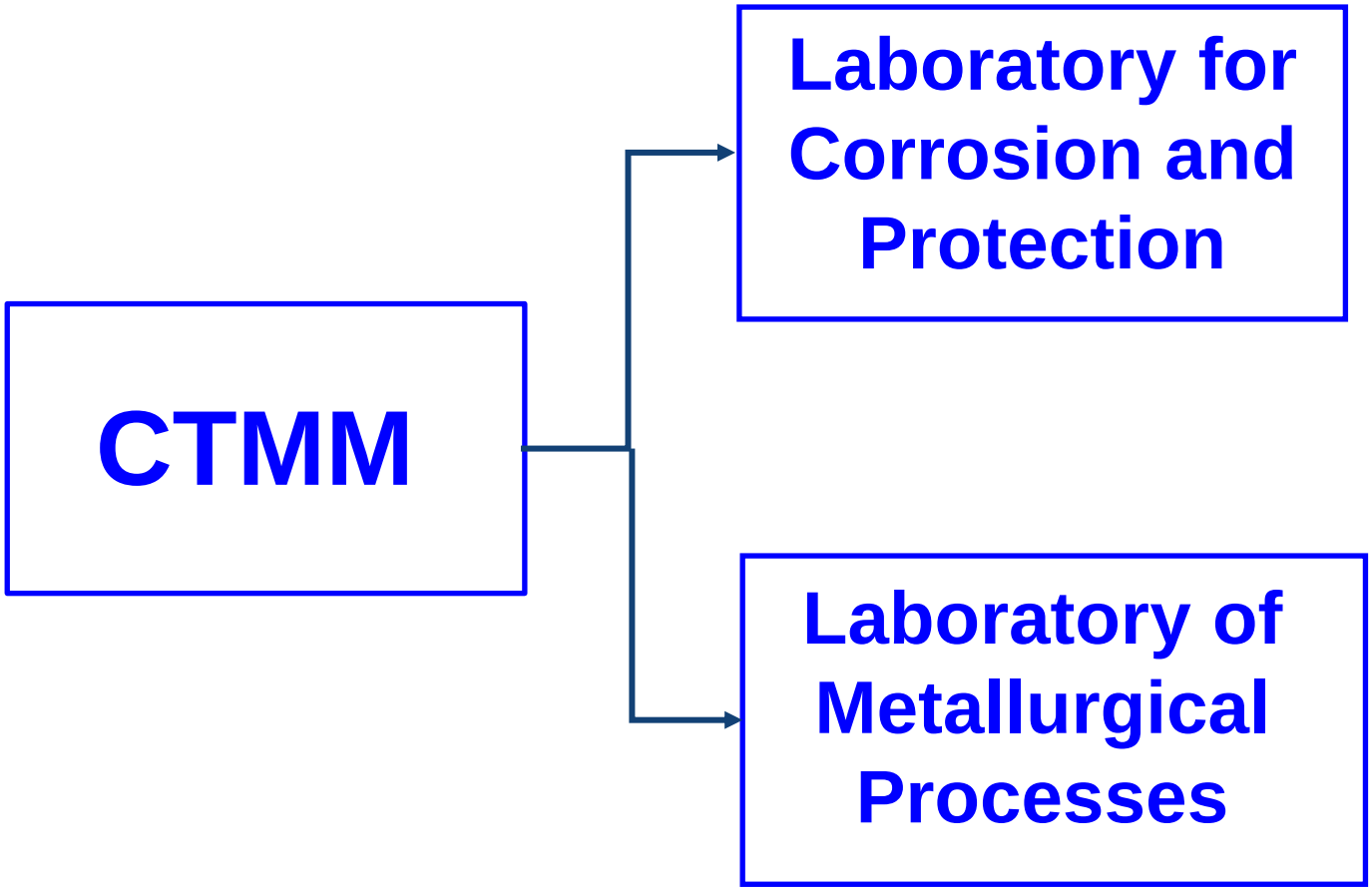
Infrastructure

- Civil Works
- Buildings
- Environmental Impacts
- Mining

Technical Centers

- CTGeo
  Center for Geoenvironmental Technologies
- CT-Floresta
  Center for Forest Resource Technology
- CTMM
  Center for Technology in Metallurgy and Materials
- CETAC
  Center for the Built Environment
- CQuiM
  Center for Chemistry and Manufactured Goods
- CTMetro
  Center for Mechanical, Electrical and Fluid Flow Metrology
- CT-Obras
  Center for Infrastructure Work Technology
- CIAM
  Center for Information Technology, Automation and Mobility
- CTMNE
  Center for Mechanical, Naval and Electrical Technologies
- NT – MPE
  Nucleus for Technological Support to Medium and to Small Enterprises
- NT- BIONANO
  Nucleus for Bionanomanufacturing
- LEL
  Light Weight Laboratory

ipt INSTITUTO DE PESQUISAS TECNOLÓGICAS


CTMM
Laboratory for Corrosion and Protection
Laboratory of Metallurgical Processes

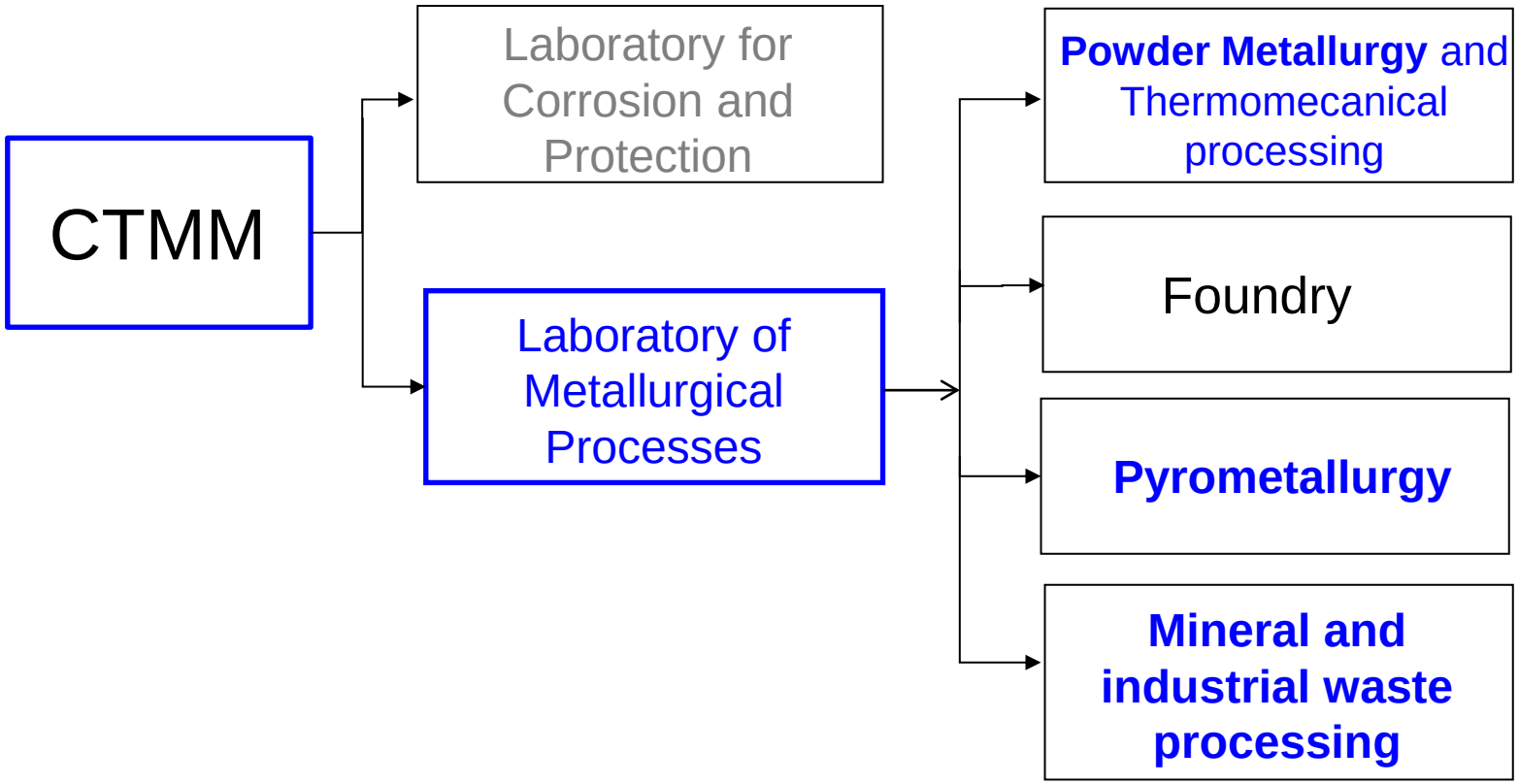
CTMM-Figures

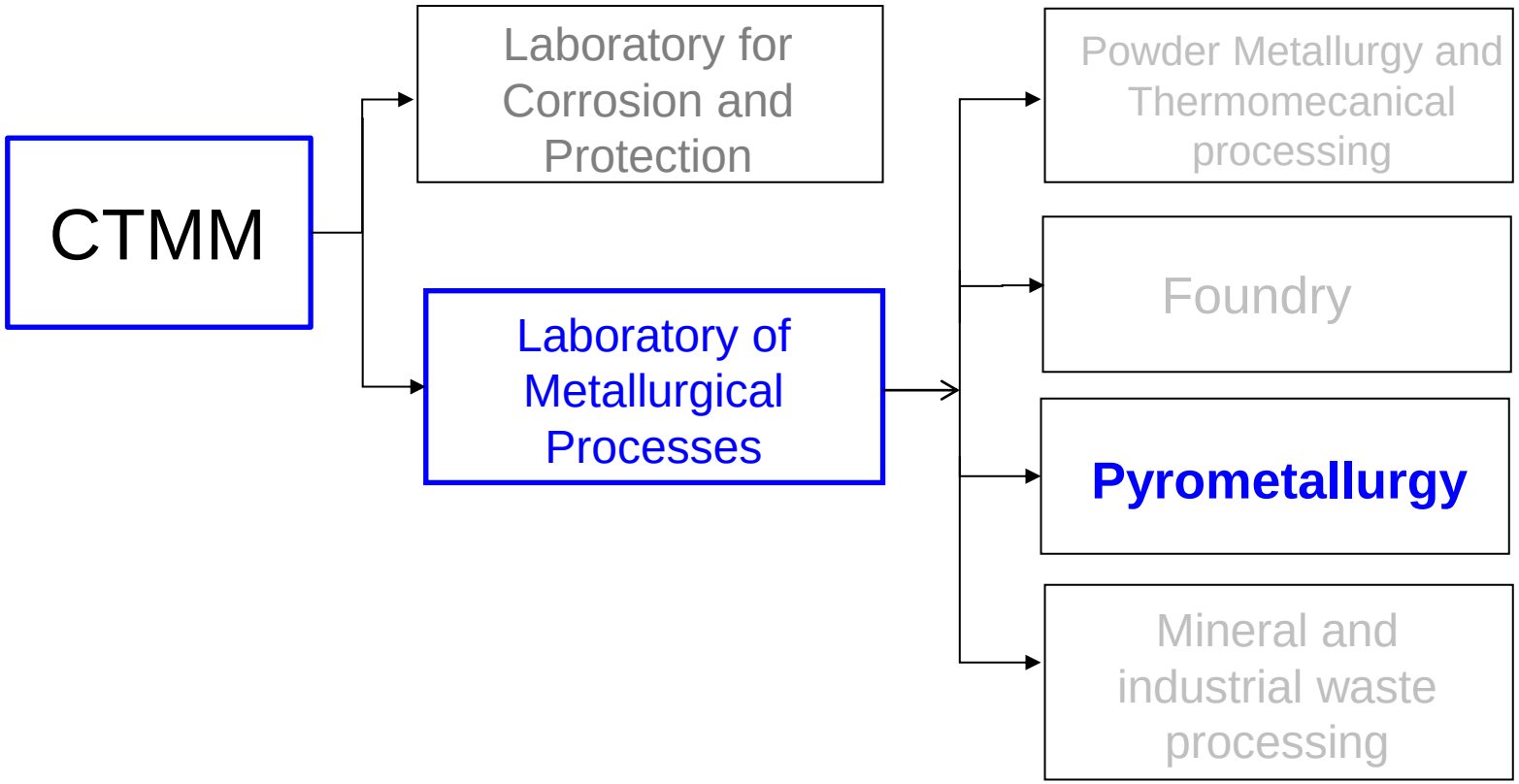
Human Resources Dec. 2015	
PhD	12
MSc	15
Undergraduate	11
Technicians	35
Administrative	4
Interns	18
Total	95

ANNUAL BUDGET (2015)
US$ 3.5 million

1.00 USD = 3.9042 BRL

ipt INSTITUTO DE PESQUISAS TECNOLÓGICAS





Laboratory of Metallurgical Processes - LPM

Experimental Facilities

- Induction Furnaces (air and vacuum): 15 kW (5 kg) - 135 kW (500 kg)
- Vacuum Induction Furnace with directional solidification device (5kg; 20 kW)

- Electroslag Remelting - ESR (ϕ 6” x 800 mm) – composite rolling mill – alloy of core distinct from alloy of surface
- Graphite Resistance Furnace (up to 2000° C) controlled atmosphere
- Experimental Rolling mill

Laboratory of Metallurgical Processes - LPM

Experimental Facilities

•EAF - 400 kW (1 ton)

- Three phase EAF
- System for oxygen and argon injection
- Temperature control
- Celox (Slac – %FeO) and oxygen activity in steel bath
- Bag house

- Multicrystallizer Furnace – multicrystalline silicon growth (20 kg and 90 kg)

•Steel centrifugation (100 kg steel)

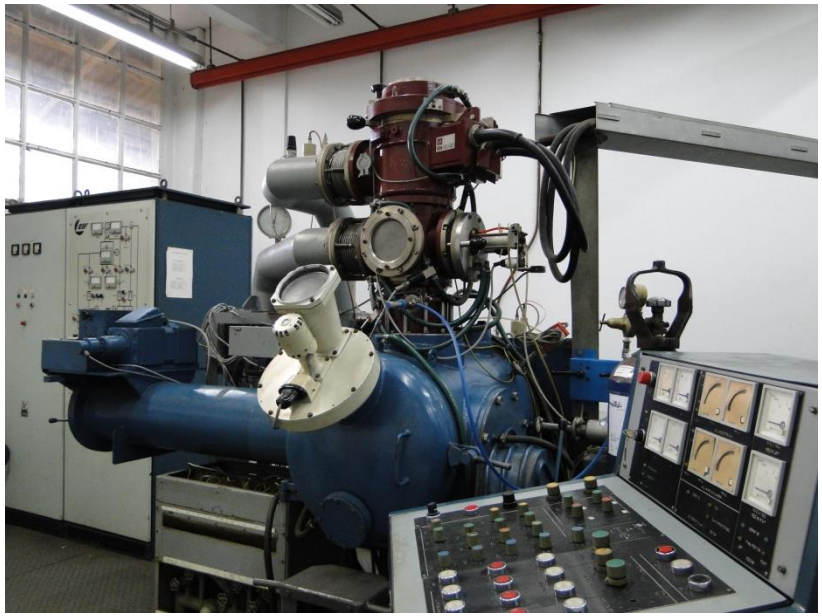
•Submerged Electric Arc Furnace - 30 KVA

ipt INSTITUTO DE PESQUISAS TECNOLÓGICAS

Laboratory of Metallurgical Processes - LPM

Experimental Facilities

- Electron Beam Furnace (EB) - 80 kW



- Laboratory Rotary Kiln Furnace (up to1500° C)

Laboratory of Metallurgical Processes - LPM

Experimental Facilities

Equipments for special experiments:

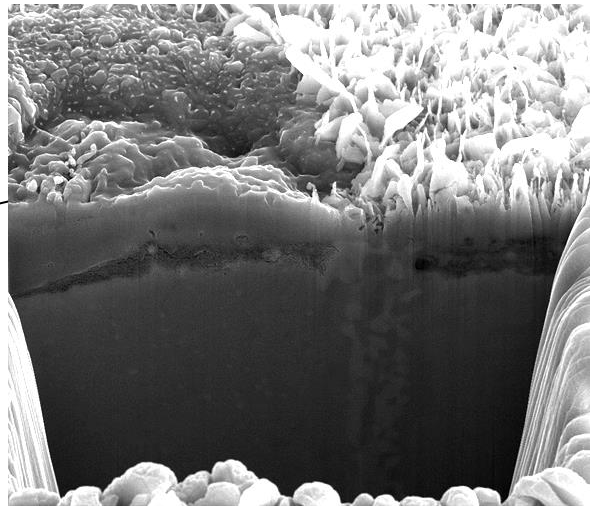
- Differential Thermoanalysis and Thermogravimetric (DTA, DSC, TG) up to 1600°C or 2000°C.
- Processes gases analyses by chromatography and mass spectrometry.

Chemical Analyses

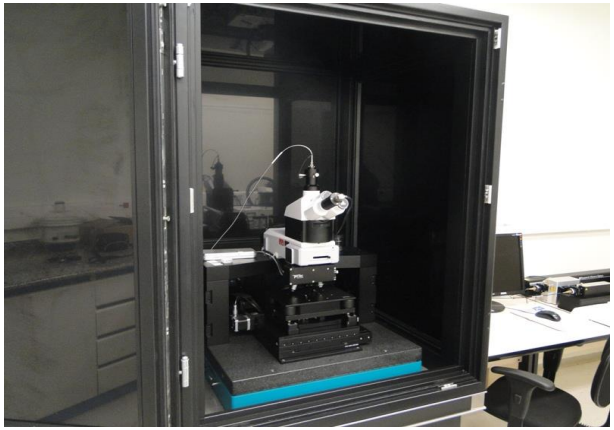
- Clean room – ISO Class 8
- Spectrophotometry of Atomic Absorption
- LECO (C, S, O, N, H).
- ICP e X-Ray Fluorescence
- XRD
- Microstructural characterization
  Optical and SEM (WDS-EDS)

Characterization techniques

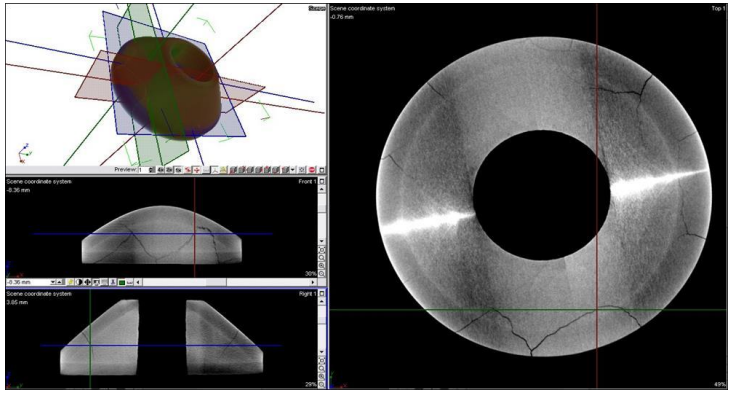
SEM FEG/FIB



Oxided HSS for rolls (surface and cross section)



Raman spectroscopy



X-ray microtomography

INSTITUTO DE PESQUISAS TECNOLÓGICAS

Pyrometallurgy

Main Activities

- Melting and Refining of Special Materials
- Carbothermic and Metalothermic reduction of Slags, Ores and Concentrates
- Modeling and determination of thermodynamic parameters of Metallurgical Processes

Pyrometallurgy

Examples of ongoing and developed projects

- Inclusions controlling in steels
- Metallurgical route for solar grade silicon production
- Ni recovery from scraps and metallurgical by-products
- Titaniferous slag production by ilmenite concentrate reduction in self-reduction pellets
- Modification of molten Steel slag (BOF) for cement application
- DeP of Mn steels and stainless steels under reducing conditions (P removed as a Phosphide)

Pyrometallurgy

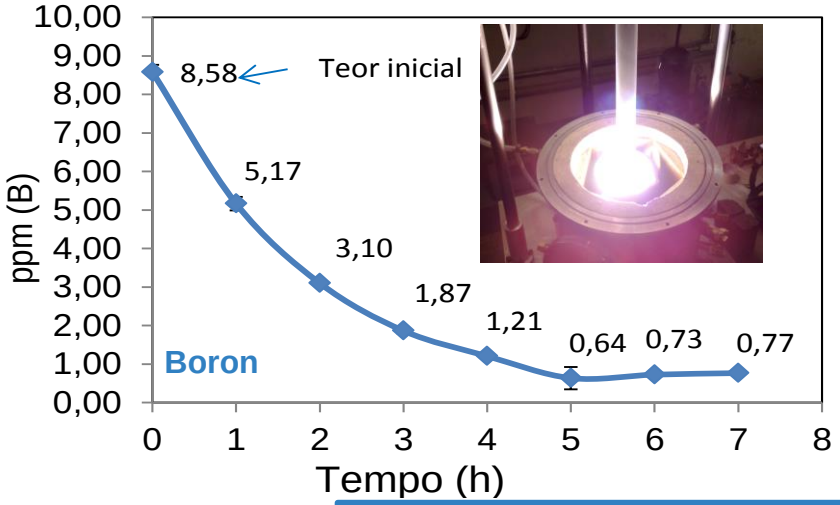
Examples of ongoing and developed projects

- Development of the route of Nb concentrate refining by selective carbothermic reduction – CBMM
- Study of aluminothermic reduction of liquid niobium concentrate
- Evaluation of the Fe-Nb dissolution in cast irons and steels (effect of particle size and Temperature on the dissolution kinetic)

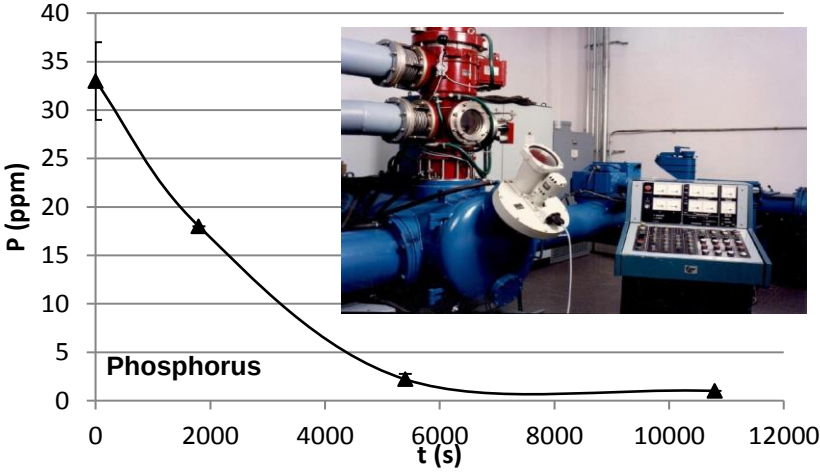
- Thermodynamic Modelling and simulation (FactSage and Thermocalc):
  - Evaluation of inclusions formation in steels
  - Simulation of reduction of the electric arc furnace dust (Zn recovery)
  - Simulation of Metalothermic reduction of oxygen steelmaking slags
  - Simulation of Hydrogen removal from steel during ladle vacuum treatment

Pyrometallurgical refining – SG Silicon

Plasma/IF furnace



EB furnace

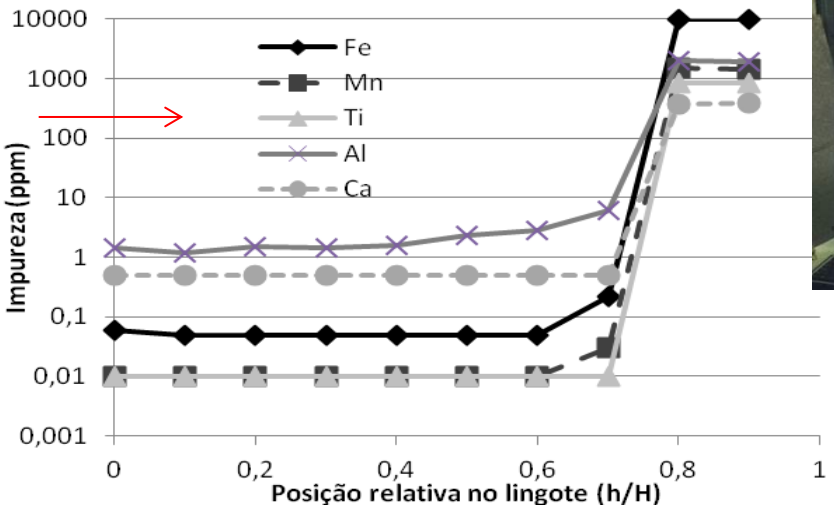


MG Silicon
98%-99%

→

SG Silicon
> 99,999%

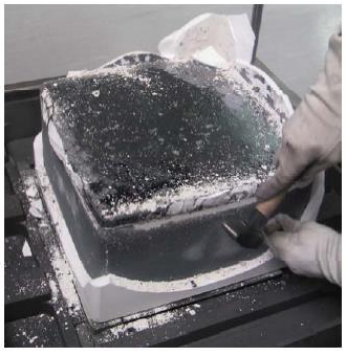
Controlled solidification



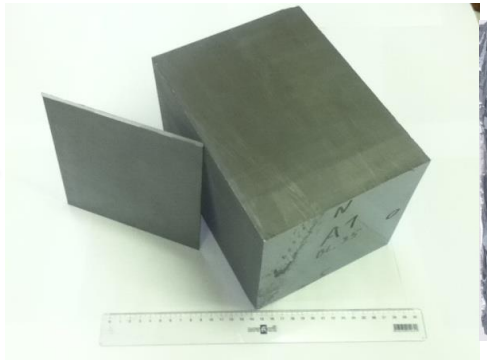
Pyrometallurgical refining – SG Silicon

SG Silicon (20 kg)

Directional solidification furnace



SG multicrystaline Silicon



Columnar grains

Blast Furnace slag X Steel Slag → Cement Industry in Brazil

- Near future scenario: There will be a shortage of BF slag to supply the demand of cement manufacturing in Brazil.

- The steel production in Brazil has been around 32-34 millions t/y for last ten years. There is no expectation of increasing X growth of construction industry in Brazil.

- Steel slag could be an alternative as cement mineral admixture, partially substituting the BF slag.

Objective: Development of autogenous process of liquid Steel Slag modification aiming its application as raw material in the portland cement manufacturing, partially substituting the BF slag

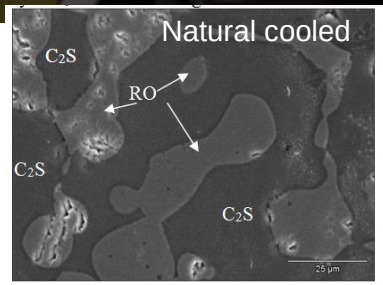
Technological barriers to be overcome:

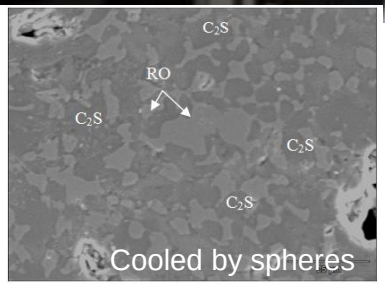
- Chemical composition modification (decreasing of free CaO and MgO, Fe2O3/FeO and Fe)
- Transformation of mineralogical phases (appropriate phases with hydraulic activity for cement production)
- Low cost by-products/residues must be used as transforming agents (achieve economic feasibility)
- Use of heat content in SSlag for modification process

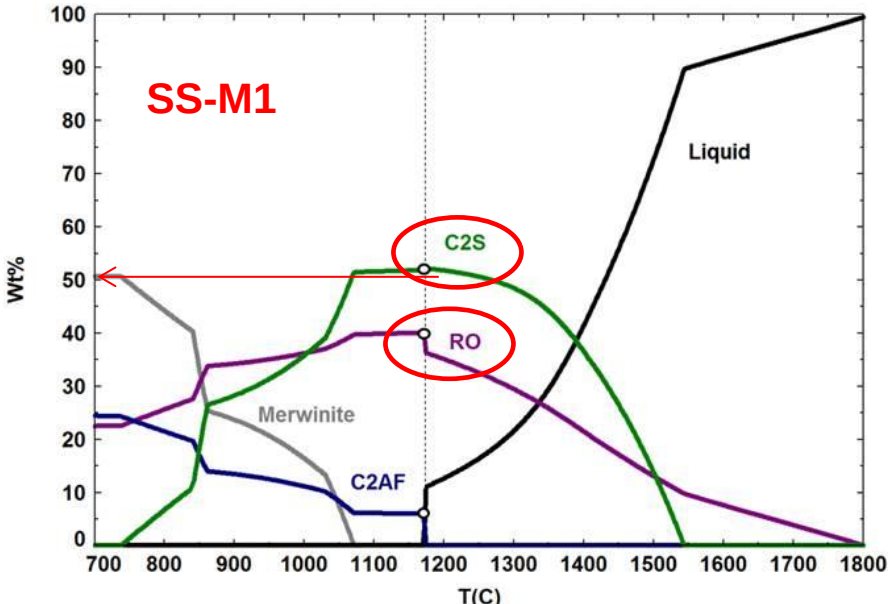
Effect of cooling rate and chemical composition on slags crystallization

Pilot Scale
(300 kg modified slag)

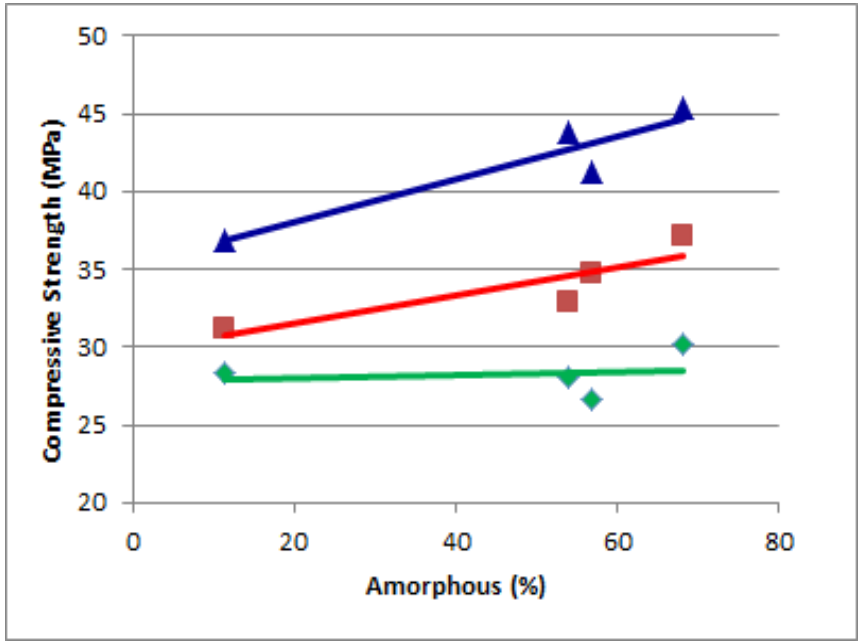
Cooling Simulation

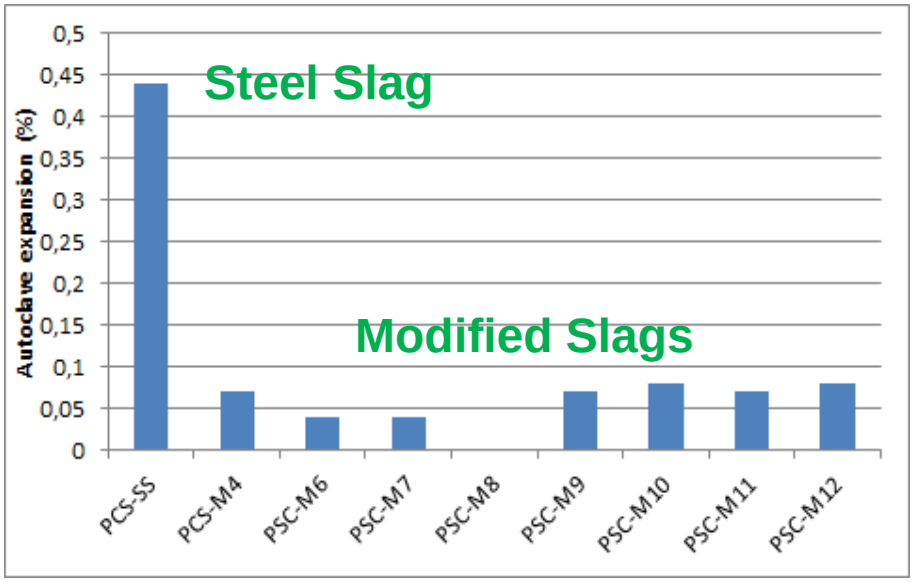


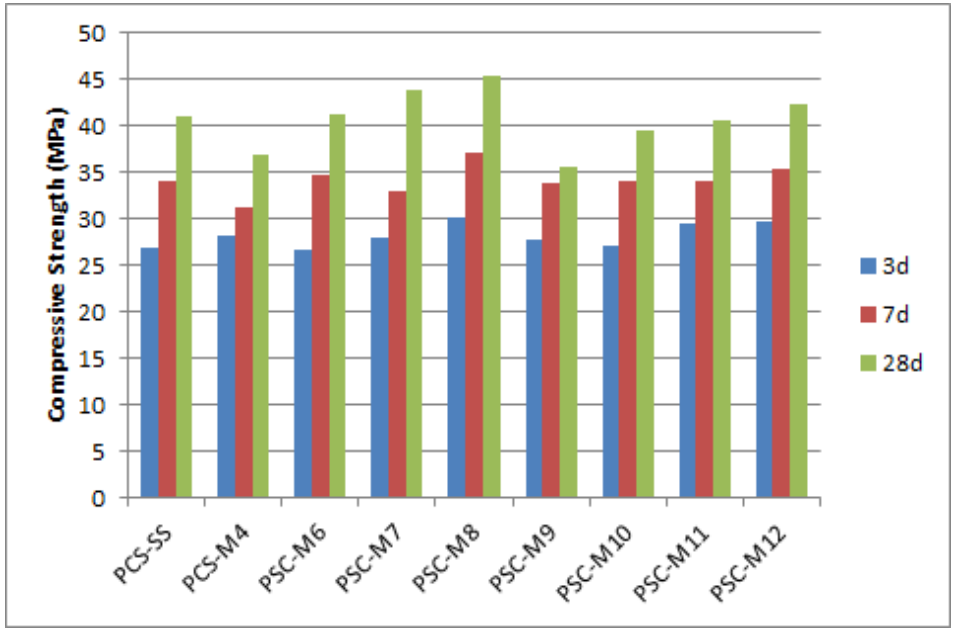




75% of ordinary Portland cement + 25% of slag (SS and modified slags)

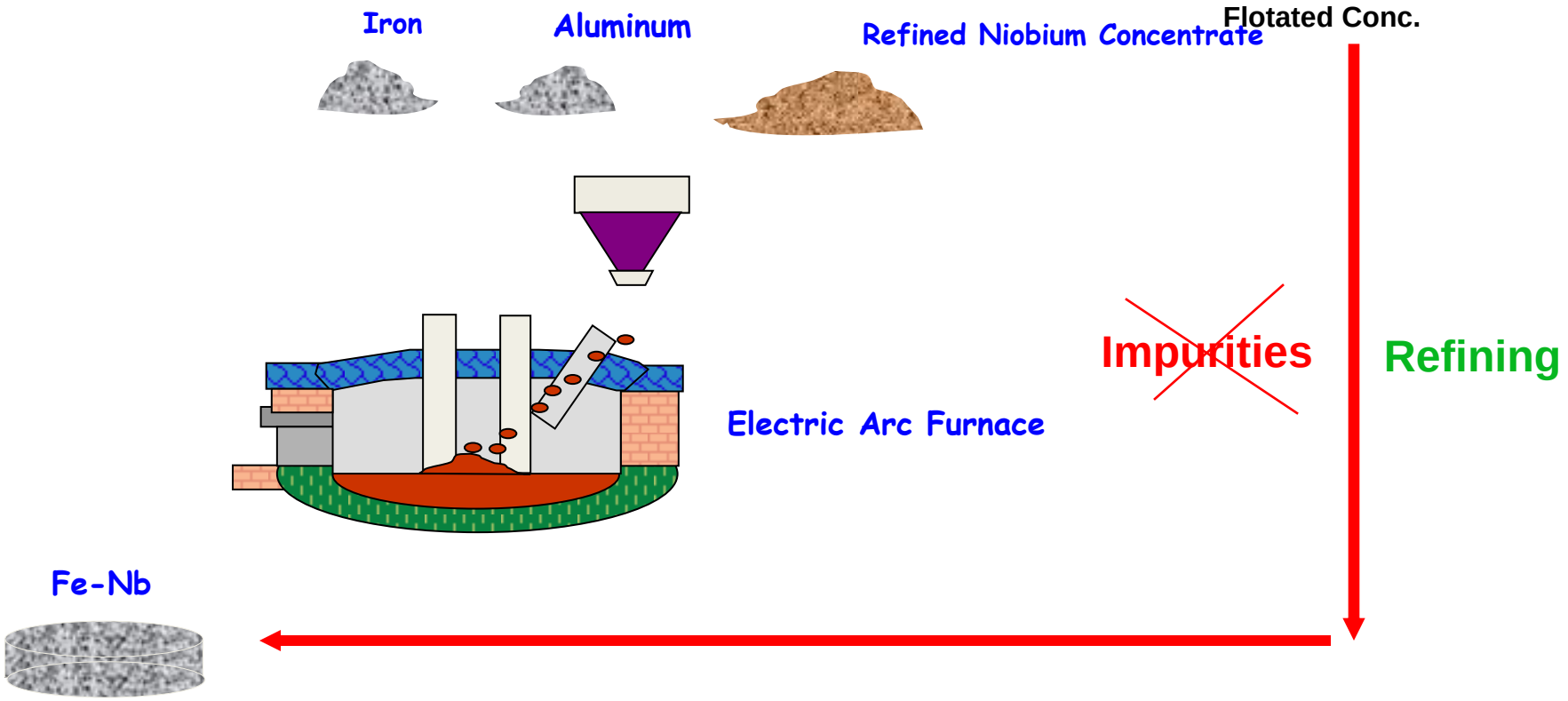






Refining of Nb concentrate by selective carbothermic reduction

Nb_2O_5 (%)	CaO (%)	**P (%)**	**Pb (%)**	SiO_2 (%)	BaO (%)	ThO_2 (%)	**Sn (%)**	**Fe_2O_3 (%)**	S (%)	H_2O (%)
55-60	0-0,2	**0,3-0,8**	**0,2-1**	0,1-0,5	15-18	2-3	**0,1**	**2-8**	0,02-2	5-7



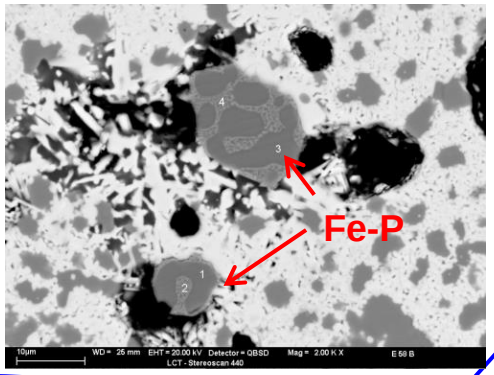
Refining of Nb concentrate by selective carbothermic reduction

Nb_2O_5 (%)	CaO (%)	**P (%)**	**Pb (%)**	SiO_2 (%)	BaO (%)	ThO_2 (%)	**Sn (%)**	**Fe_2O_3 (%)**	S (%)	H_2O (%)
55-60	0-0,2	**0,3-0,8**	**0,2-1**	0,1-0,5	15-18	2-3	**0,1**	**2-8**	0,02-2	5-7

Conc. Flotado.

Refining

Carbothermic reduction of Nb concentrate



Reduction of P, Pb, Sn, (Fe)
Prevent Nb reduction

Refined concentrate

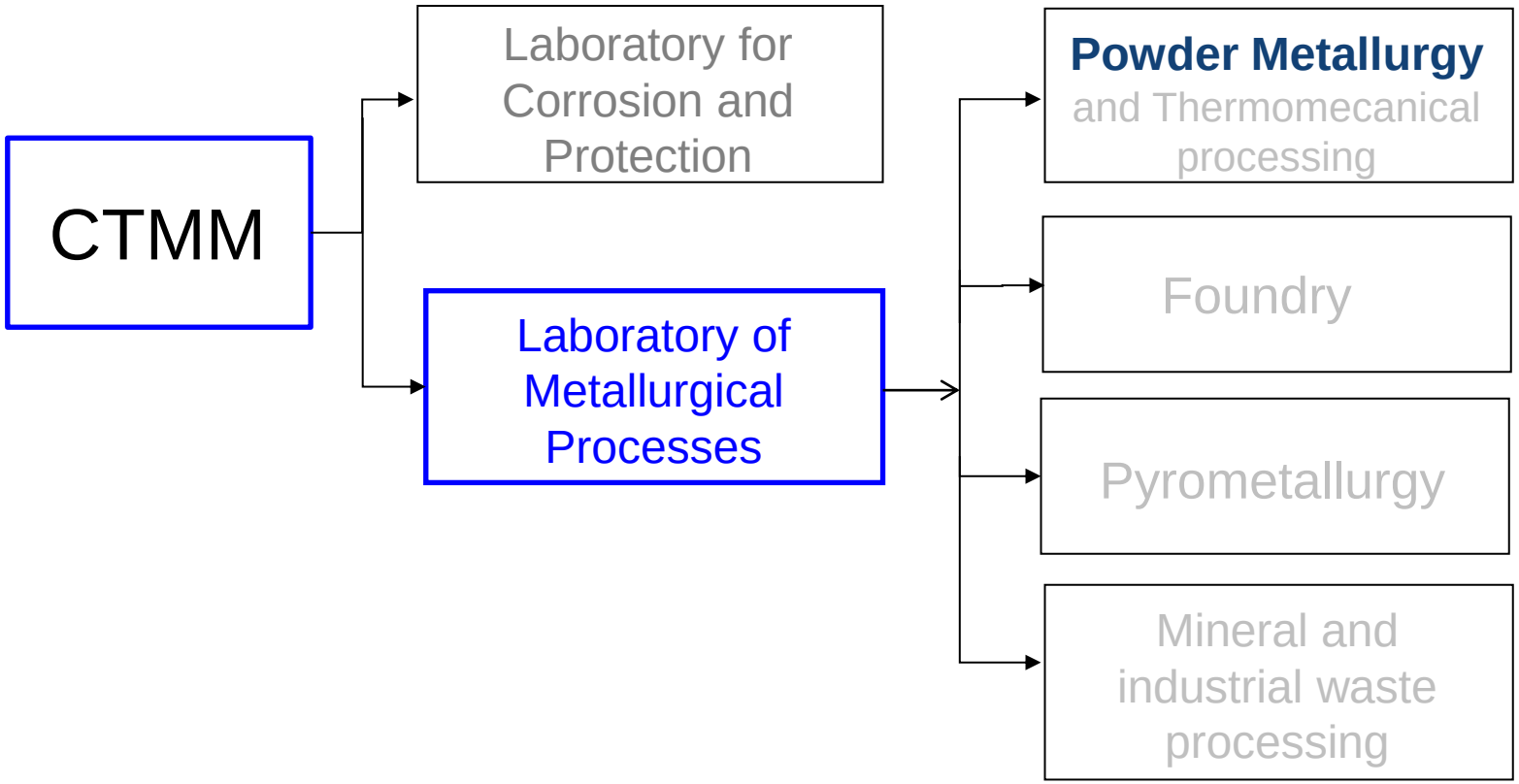
Fe-P-Sn; Pb

Melting and metallic phase (Fe-P alloy) separation from refined concentrate

Pilot scale (300 kg by batch) in EAF
> 40 t of Nb conc. refined at IPT

Process adopted by CBMM since 2000
Capacity ~ 80.000 t conc DeP/y

ipt INSTITUTO DE PESQUISAS TECNOLÓGICAS


CTMM
Laboratory for Corrosion and Protection
Laboratory of Metallurgical Processes
Powder Metallurgy and Thermomecanical processing
Foundry
Pyrometallurgy
Mineral and industrial waste processing

Laboratory of Metallurgical Processes - LPM

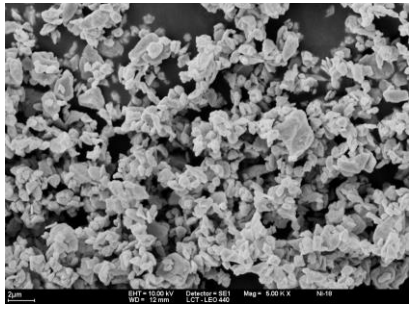
Experimental Facilities

- Powders production
  - Powder atomizers (water and inert gas)

Nb and NbO powder for capacitors

Hydriding-Milling-Dehydriding

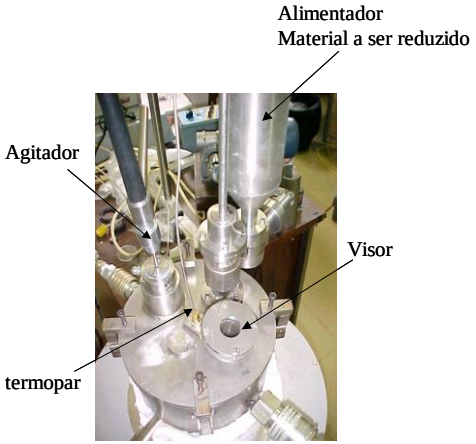
Nb (100 kg) after Hydriding

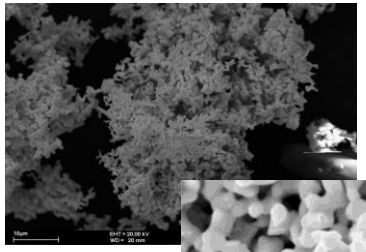


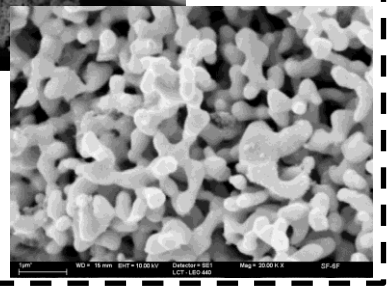
$Nb_2O_5 + 5\,Ca = 2\,Nb + 5\,CaO$

Molten Salt: $CaCl_2$

High Ca and CaO solubility

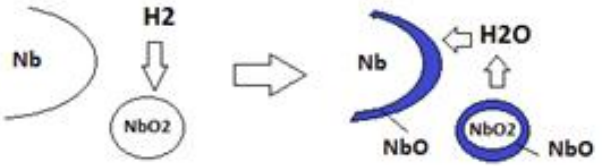


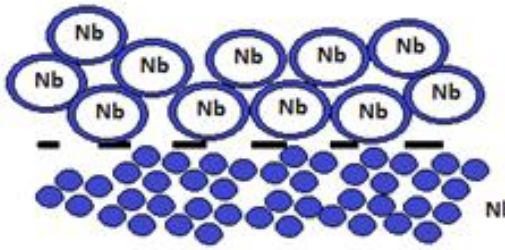


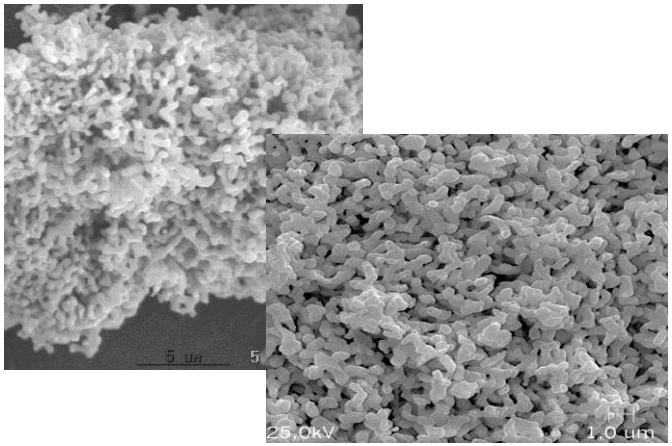


$Nb_2O_5 + H_2 = 2\,NbO_2 + H_2O$

$NbO_2 + H_2 = NbO + H_2O$

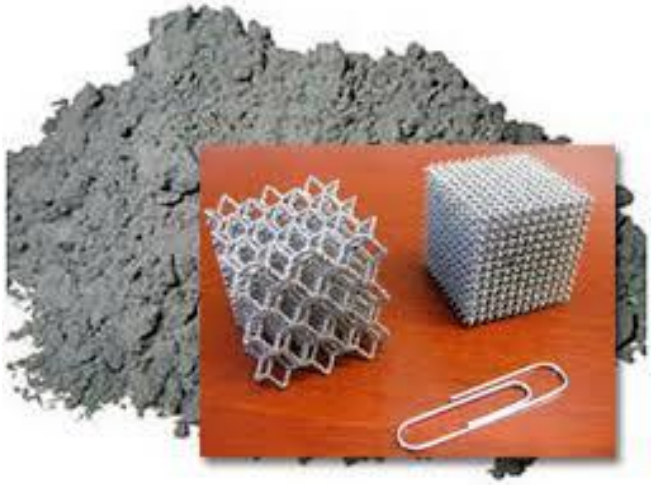




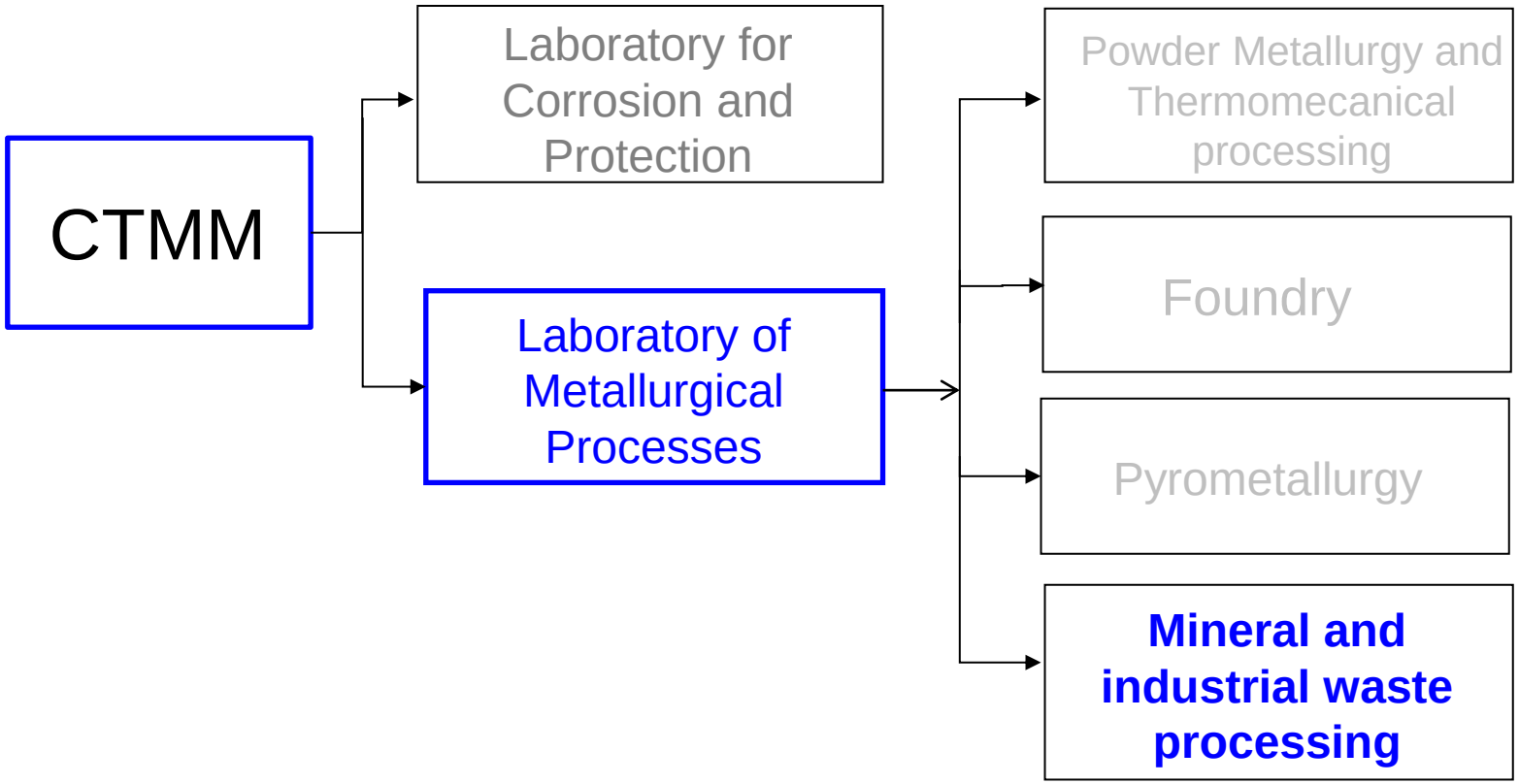


Sample	Capacitance (kCV/g)	DCL (nA/CV)
Market specification	85 ~ 105	< 0,35
Pilot plant	112 ~ 140	0,12 ~ 0,28

Ti-Nb-Zr and Nb-Ti powders for Additive Manufacturing



- **Orthopedic Implants**
- **Alloys melting in a EB furnace**
- **Powders production:**
  - **Inert gas atomization**
  - **H-DH + Milling**
  - **H-DH + Milling + plasma spherodizing**
- **Implants produced by additive manufacturing**
- **Biocompatibility tests**



Mineral and Industrial Waste Processing

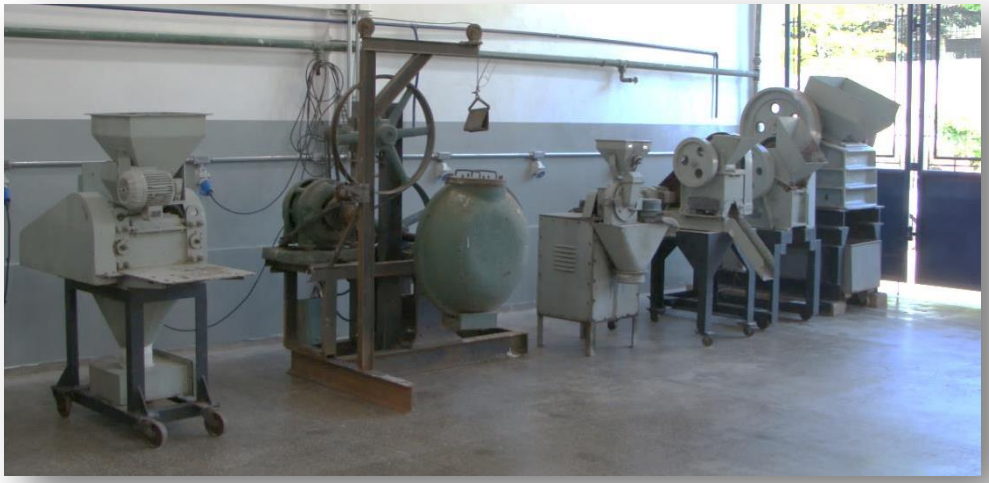
- Expertise in applying mineral processing techniques
  - Ores
  - Fertilizers
  - Industrial wastes (metallurgy, construction, agroindustrial, etc)

- Batch and pilot scales equipment
  - 450 m^2

Mineral and Industrial Waste Processing

Mineral Processing

- Comminution processes (batch / pilot)
  - Evaluation of grinding media wear
  - Assessment of chemical supplies for grinding process
  - Determination of process parameters (grinding and classification)



Mineral and Industrial Waste Processing

Mineral Processing

Enrichment processes

(ores and tailings)

- Density separation
  - Jig
  - Shaking table
  - Heavy liquid

- Flotation
  - Kinectic
  - Evaluation of chemical supplies

Mineral and Industrial Waste Processing

Mineral Processing

Enrichment processes

- Electrostatic separation
- Magnetic separation

- Classification
  - Cyclone
  - Spiral classifier
  - Air classifier

Mineral and Industrial Waste Processing

Fine particles agglomeration processes

- Binders exploration
- Process development (pelletization and briquetting)
- Biomass: physical pre-treatment and densification

INSTITUTO DE PESQUISAS TECNOLÓGICAS

Project: Nd/Di production from CBMM Didymium oxide

Next step..... Alloy and magnet production

World Reserves of RE

	Mine production[e]		Reserves[5]
	2013	2014	
United States	5,500	7,000	1,800,000
Australia	2,000	2,500	[6]3,200,000
Brazil	330	—	22,000,000
China	95,000	95,000	55,000,000
India	2,900	3,000	3,100,000
Malaysia	180	200	30,000
Russia	2,500	2,500	([7])
Thailand	800	1,100	NA
Vietnam	220	200	([7])
Other countries	NA	NA	41,000,000
World total (rounded)	110,000	110,000	130,000,000

RE Oxide basis

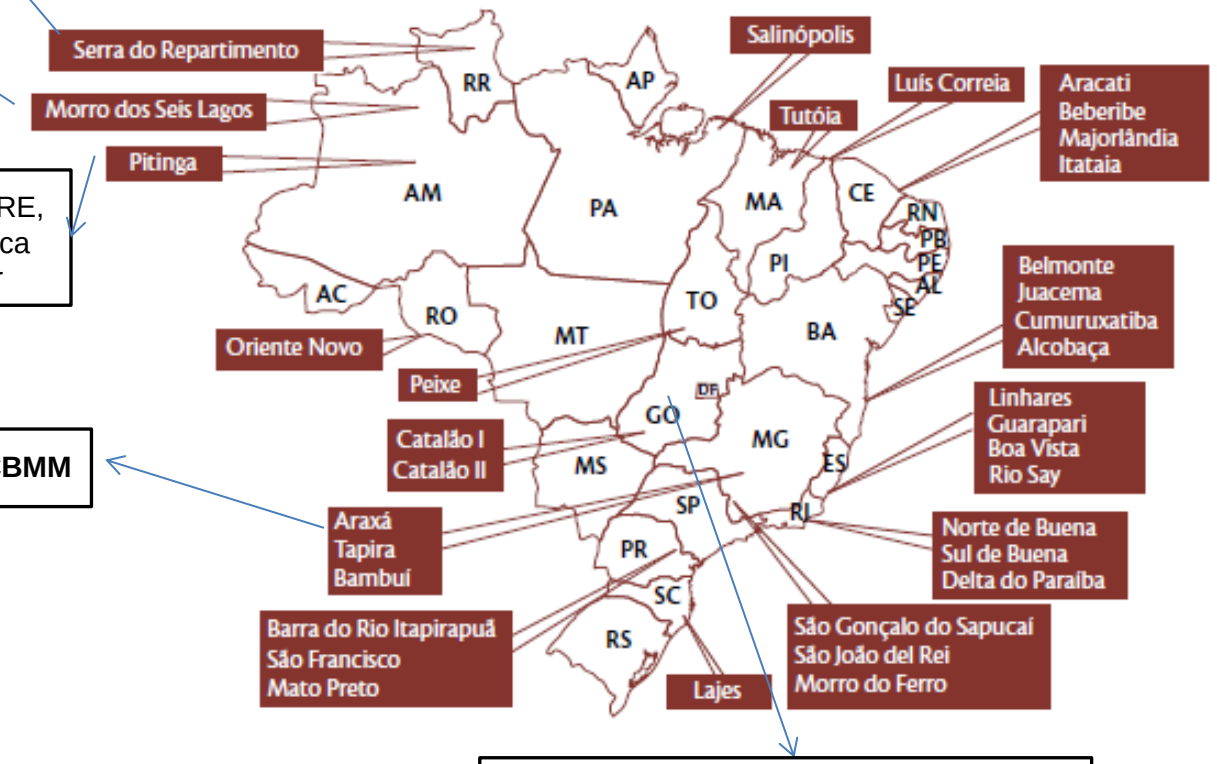
Fonte: U.S. Geological Survey, Mineral Commodity Summaries, January 2015

Domain of phosphates, with 3,2% Ce and 2,5% La (close to Indian reserves)

Biological and Indian reserve

Xenotime (1% de RE, mainly Y) – Taboca Mining - Minsur

Tailings of Nb extraction - CBMM

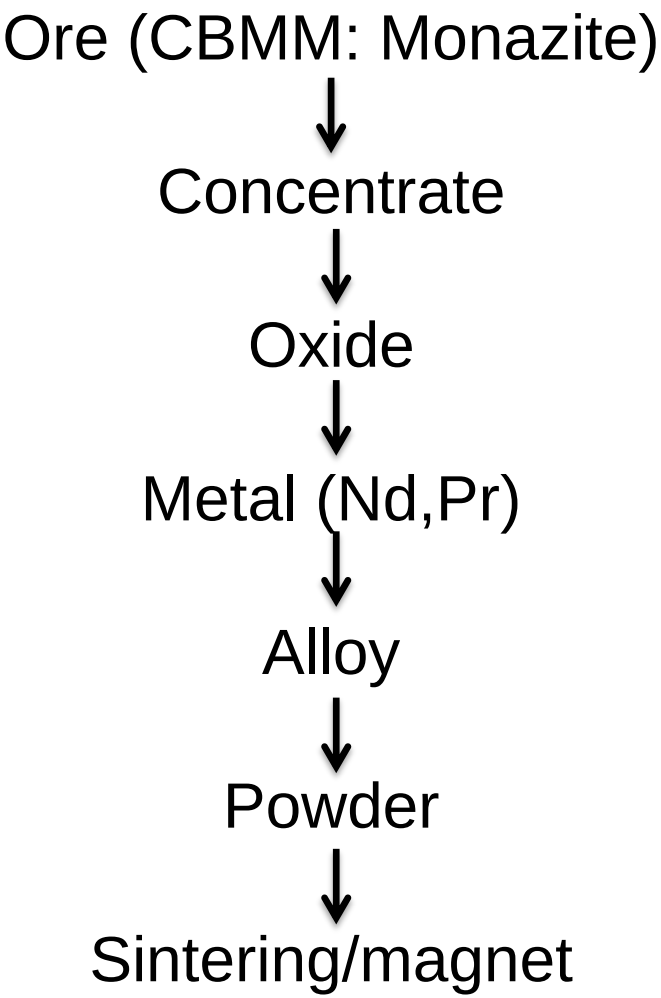


Fonte: MCTI, apresentação no CT-Mineral (2010).

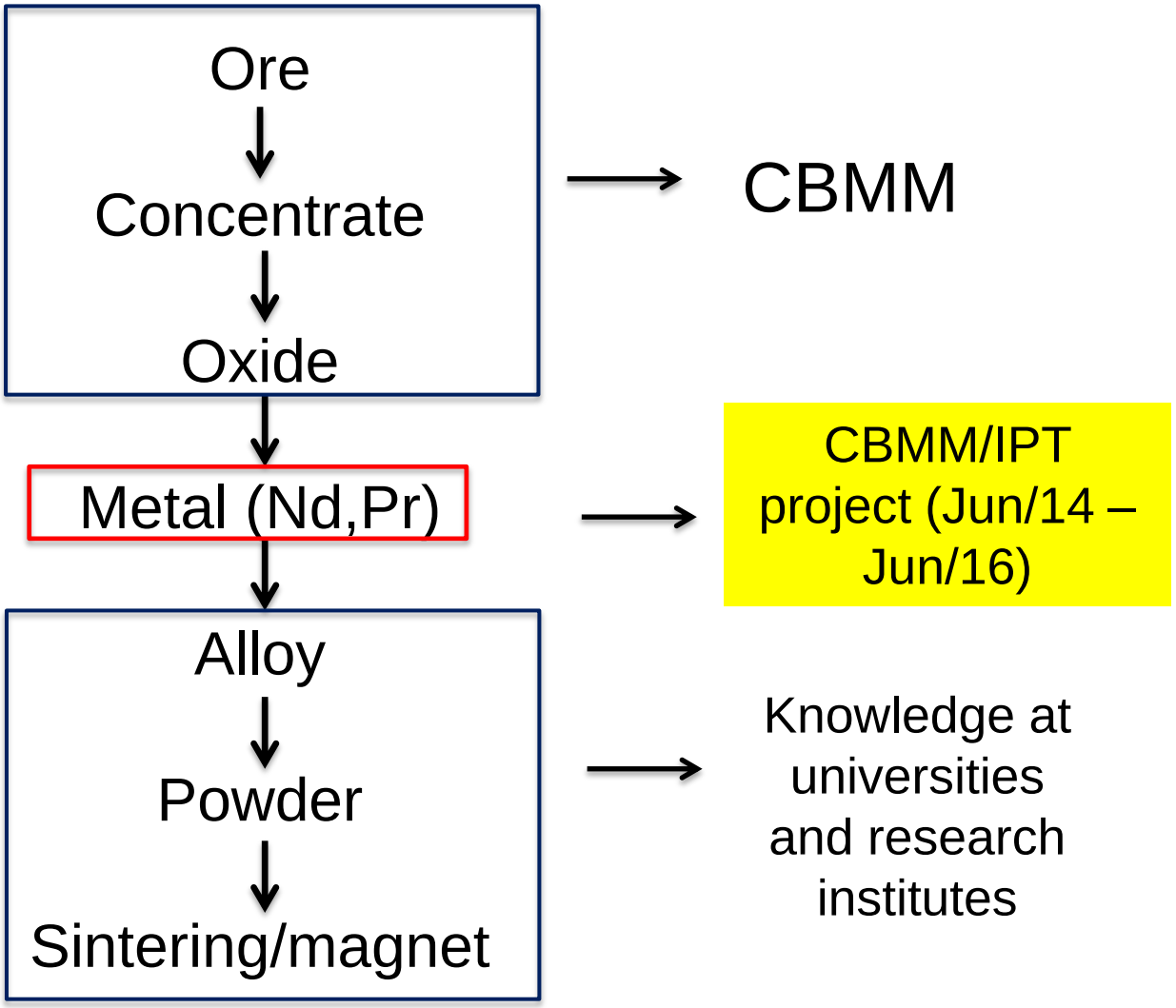
Serra Verde Mining of the Mining Ventures Brazil group (city of Minaçu – GO)

Mineral	%
Bariopyrochlore	**4**
Limonite, goethite	36
Barite	20
Magnetite	16
Gorceixite	6
Monazite	**4**
Ilmenite	5
Quartz	4
Others	5
Total	100

(Nd,Pr)-Fe-B magnets production



(Nd,Pr)-Fe-B magnets production



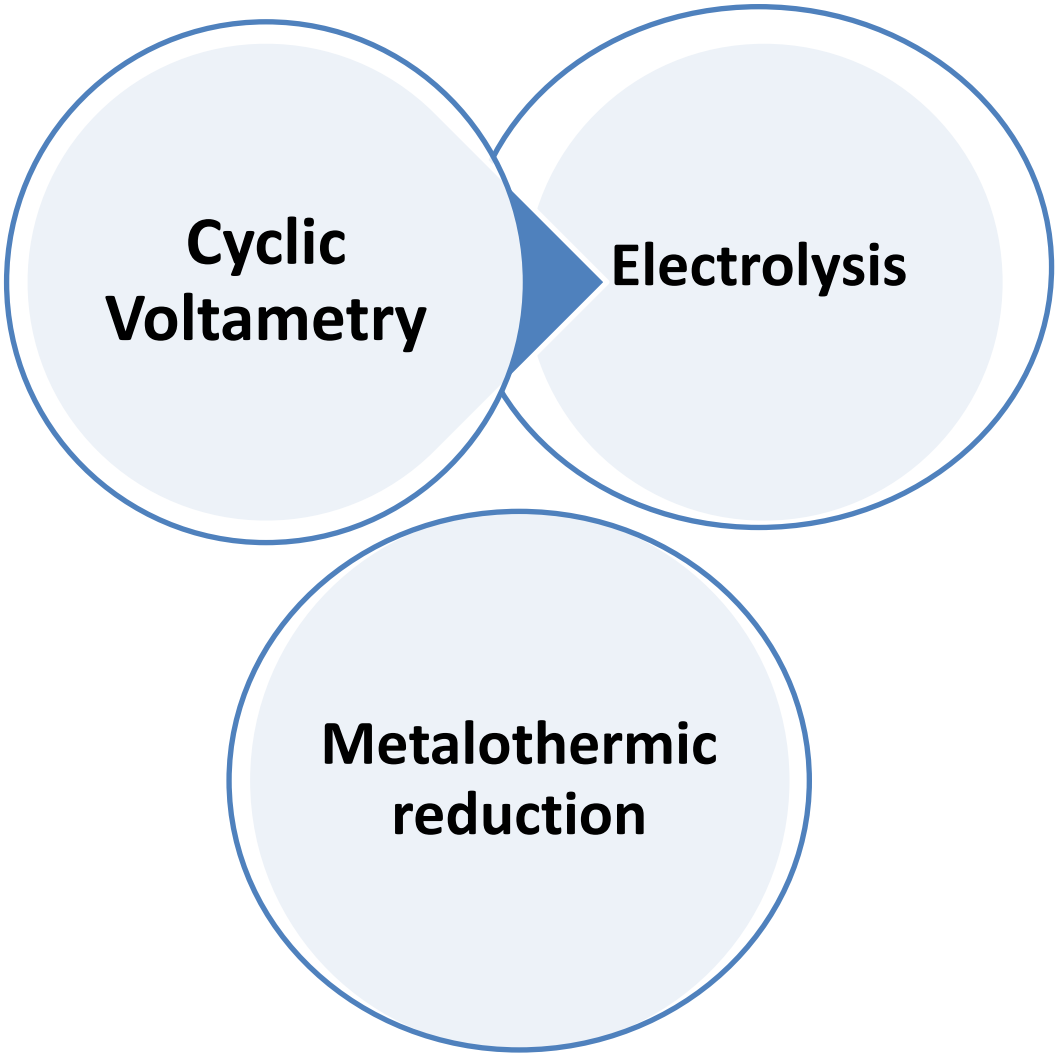
Routes investigated

Metalothermic

- Production of ingots by batch
- Consumption of reducing agent
- High reactive metals (Ca) – atmosphere controlling
- Salt cannot be recycled (depend on type of salt)

Electrolysis in molten salt

- Continuous process
- Electric energy consumption
- Consumed anodes (CO_2 + CO_2 equiv. emission)
- Salt can be recycled (only making up is necessary)



Routes definition

↓

Design of reactors

↓

Reactors construction (furnaces and automation)

↓

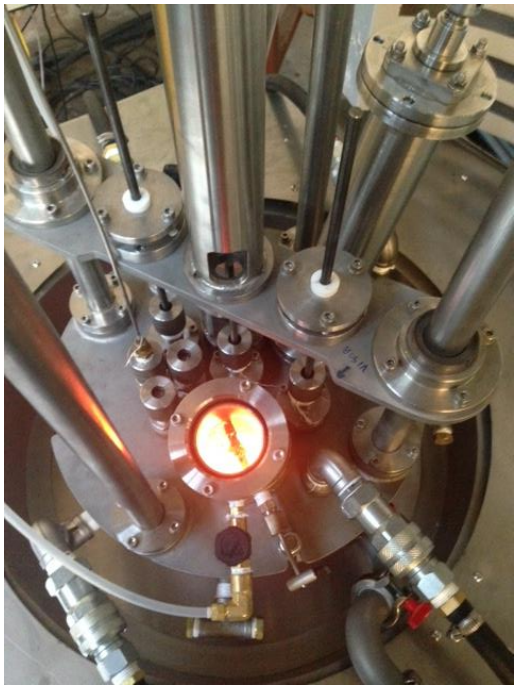
Installation and Start up

↓

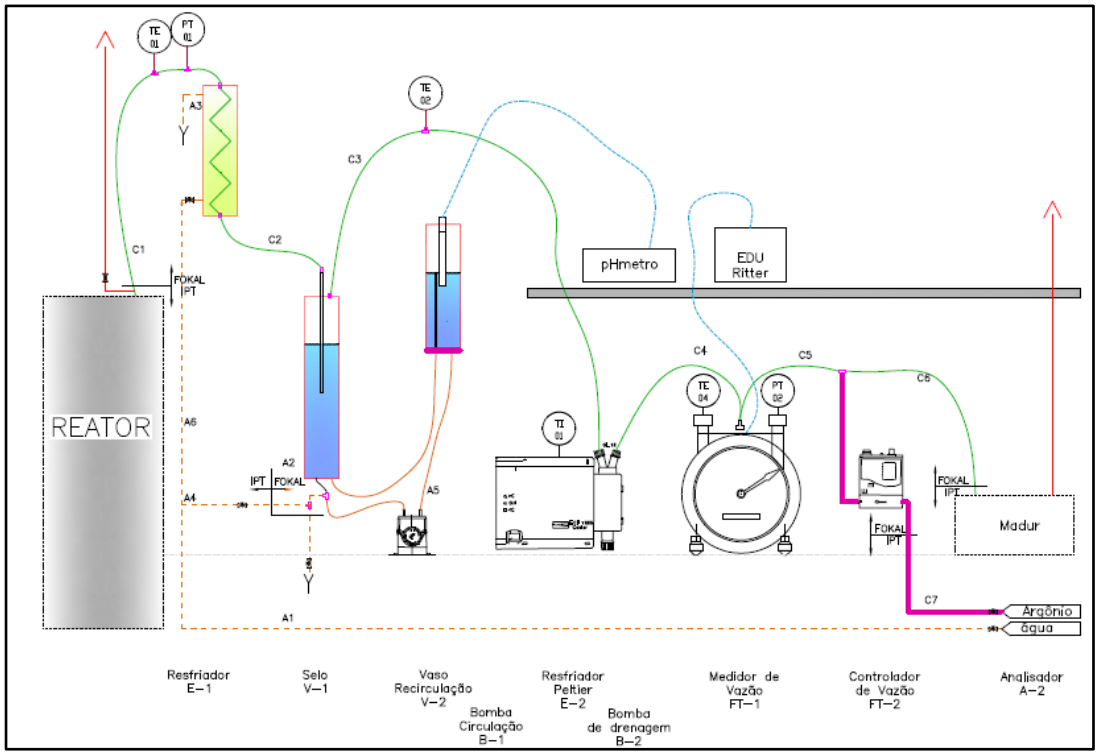
Tests

Cells and reactors

Electrolysis

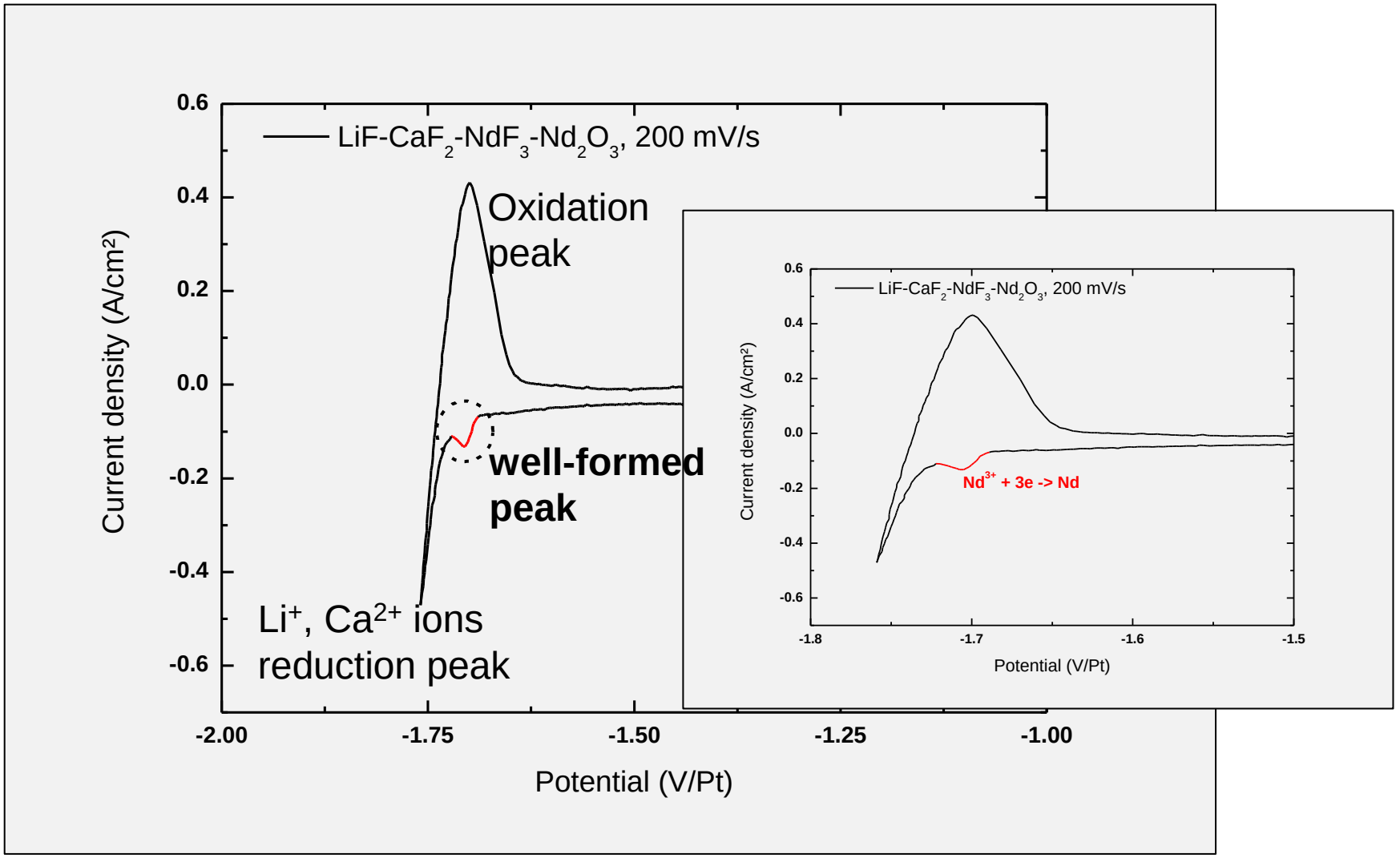


Cells and reactors



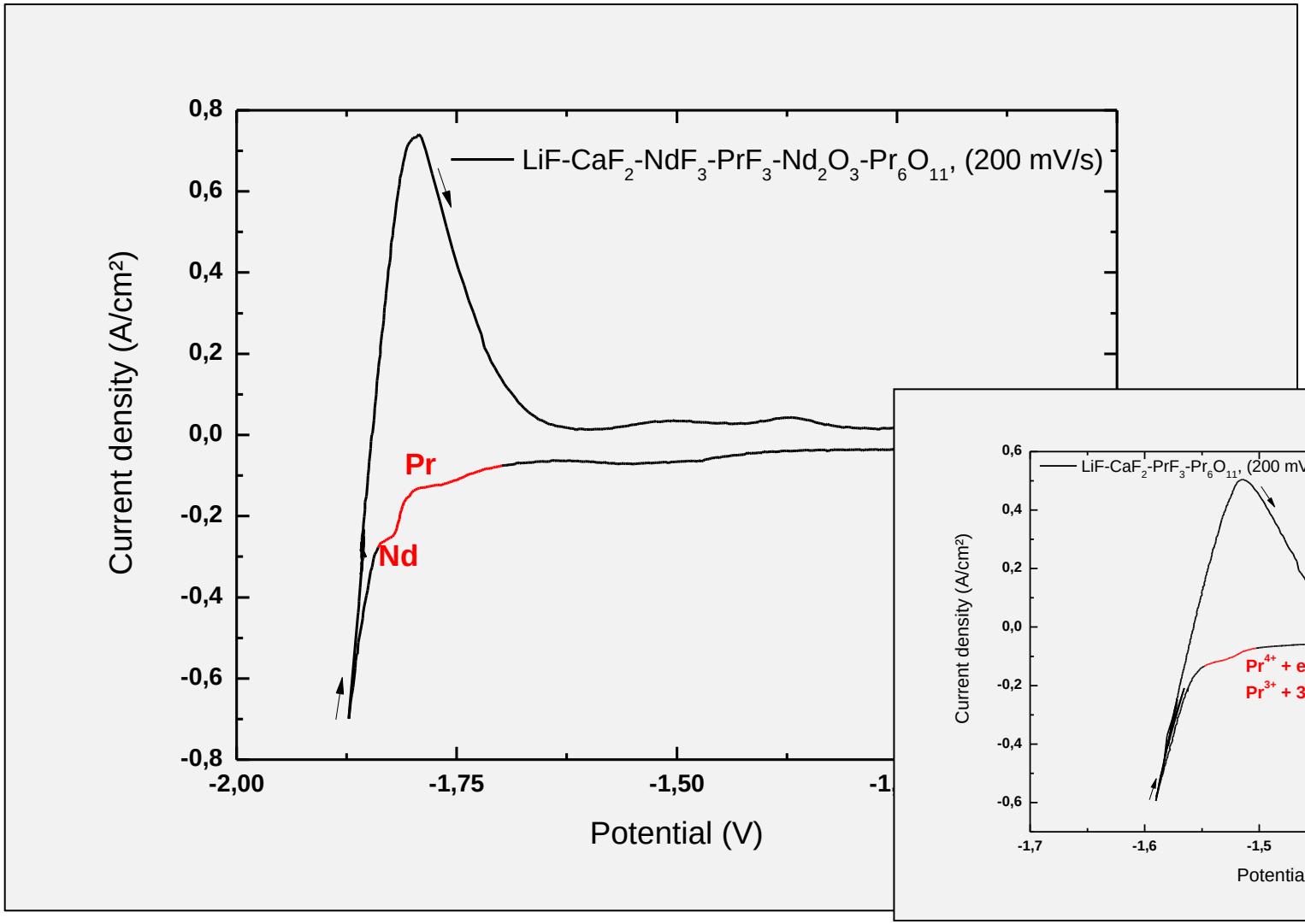
Cyclic voltammetry experiments

$LiF\text{-}CaF_2\text{-}NdF_3\text{-}Nd_2O_3$



Cyclic voltammetry experiments

$LiF\text{-}CaF_2\text{-}NdF_3\text{-}PrF_3\text{-}Nd_2O_3\text{-}Pr_6O_{11}$



Metalothermic

- **Investigated parameters:**
  - Temperature
  - Time reaction
  - Ca excess (solubility of Ca in molten salt)
  - Mixing rate
  - Ca/salt ratio

- **Results:**

  - 200 - 400 g Nd or Di/batch

  - Reduction yield: > 95%

  - Main impurity: Calcium (Removed by vacuum treatment of liquid didymium)

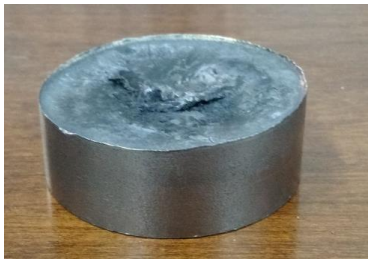
  -Other impurities similar Nd produced with Baotou oxide

Electrolysis

- **Investigated parameters:**
  - Salt composition (Fluorides – increase Di_2O_3 solubility) – wider operation window
  - Oxide feeding rate (control of O^{-2} dissolved in molten salt)
  - Oxide feeding rate x I (A) – prevent anodic effect (CFx)
  - Mixing rate
  - Temperature

- **Results:**

  - 300 - 450 g Nd or Di/batch

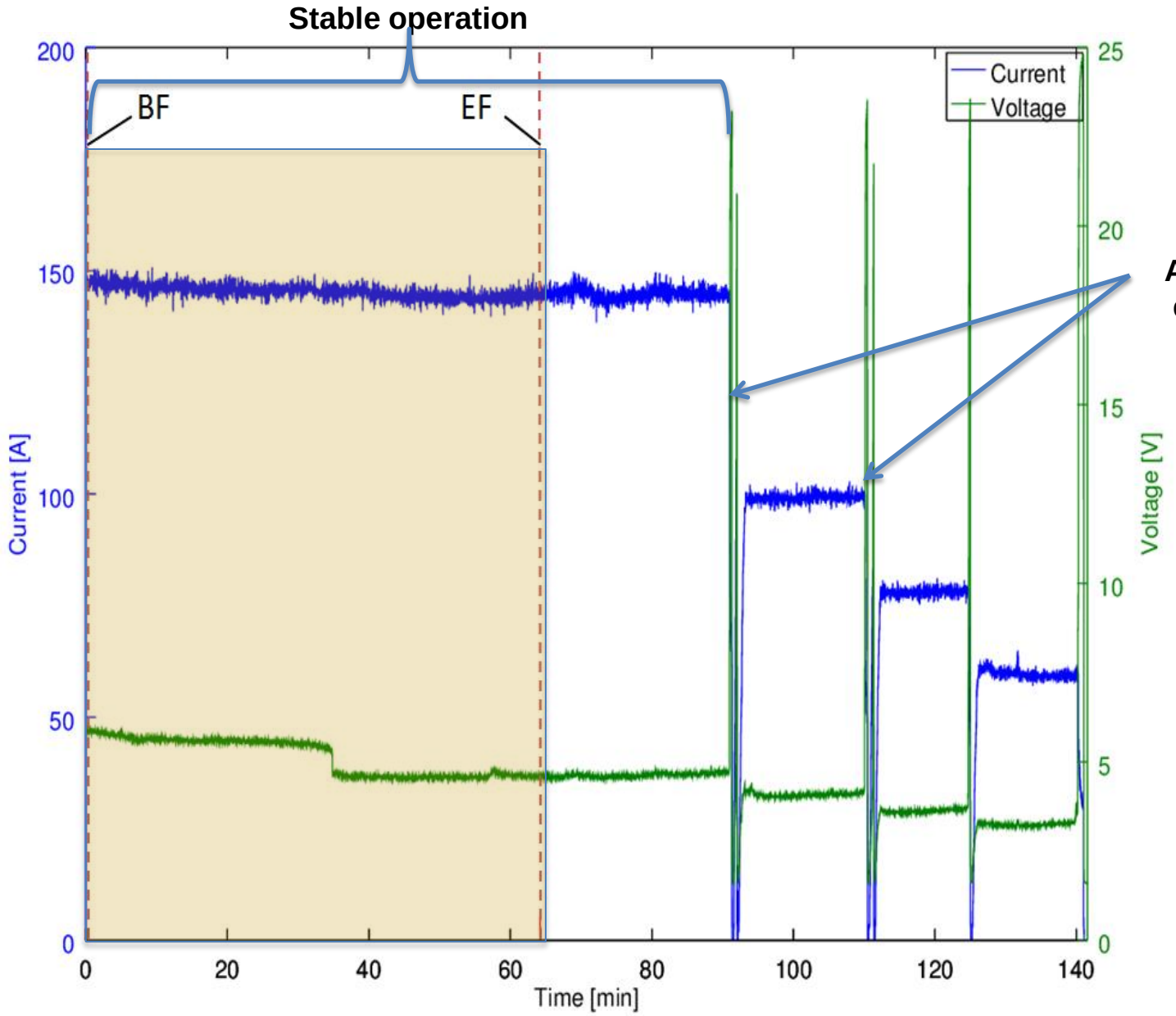


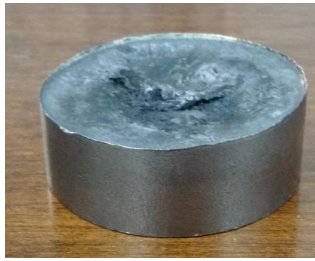
  - Current efficiency 60/70% (η = [weight produced Nd/Di]/[calculated weight Nd/Di production by I (A)] * 100

  - 4-5 Kwh/kg Nd (lab scale)

  - Impurities similar Nd produced with Baotou oxide

Electrolysis



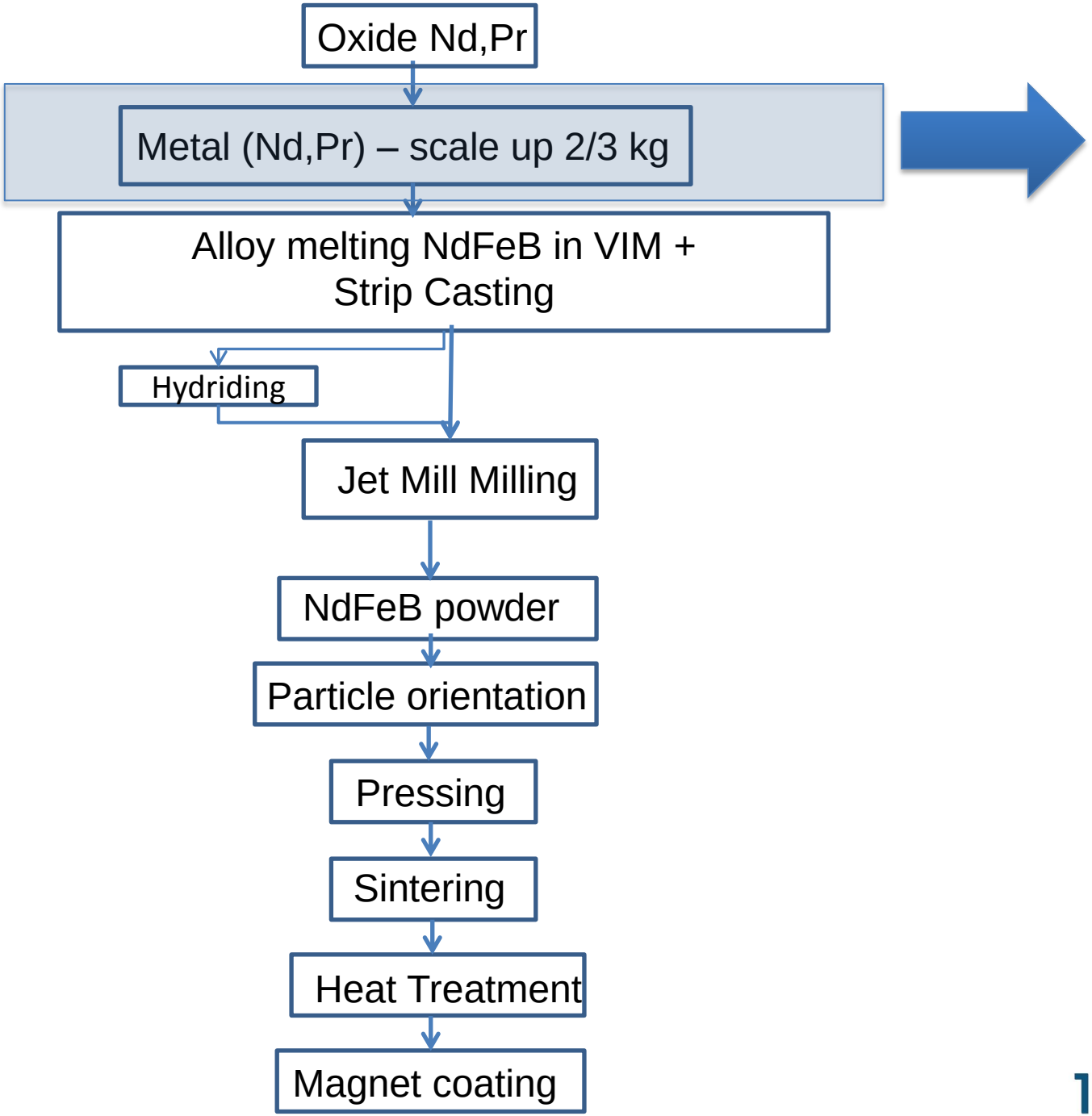


INSTITUTO DE PESQUISAS TECNOLÓGICAS

Project: Nd/Di production from CBMM oxide

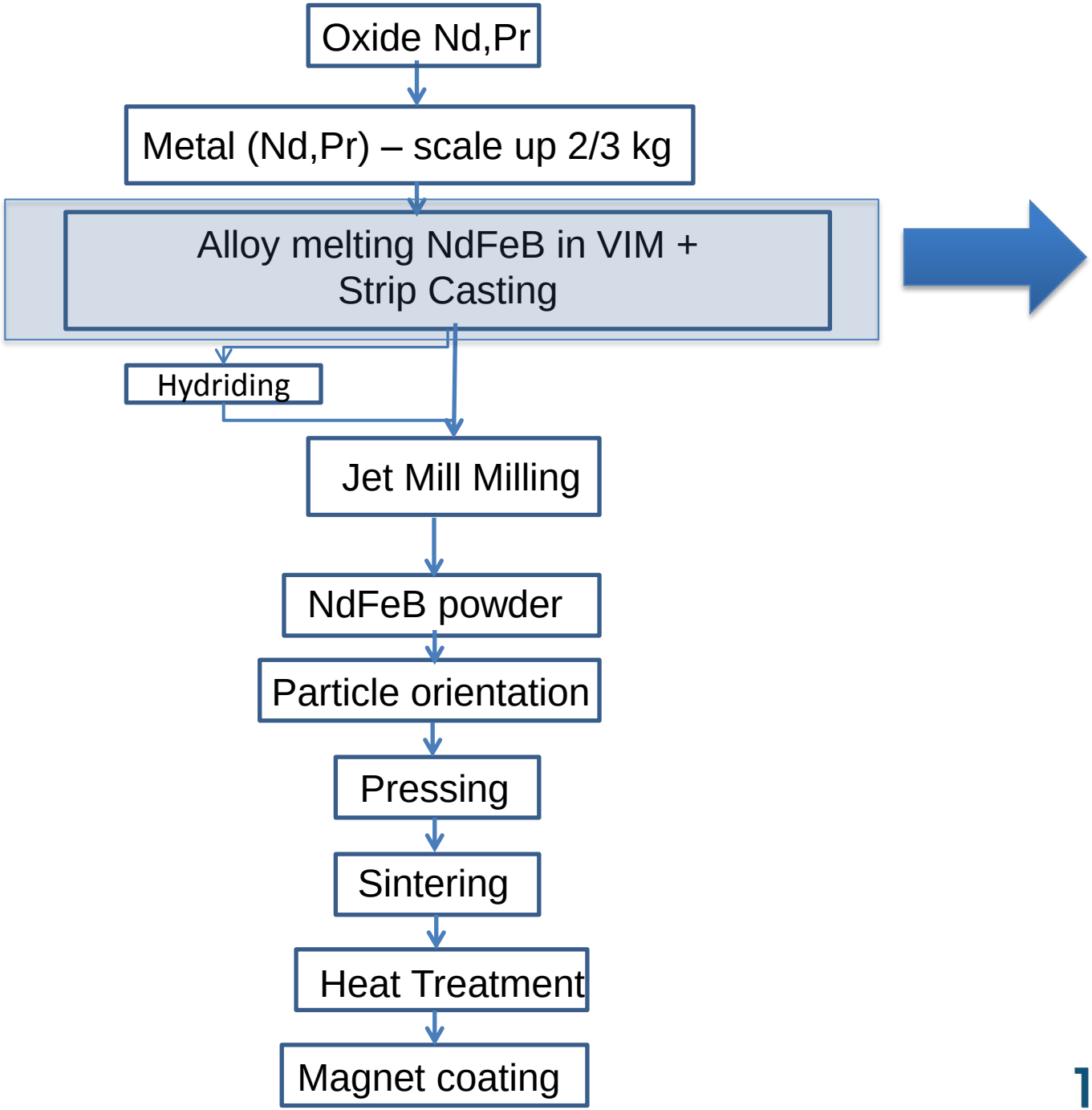
Next step..... Alloy and magnet production

INSTITUTO DE PESQUISAS TECNOLÓGICAS



Electrolysis – scale up

- **Production of 2-3 kg by batch**
- **Heating source – DC current from electrolysis**
- **Open cell**
- **Gas treatment (CF_x neutralizing)**
- **Tapping of liquid Didymium**
- **Automation for Di_2O_3 oxide feeding control (prevent anodic effect)**



VIM

Main Challenges

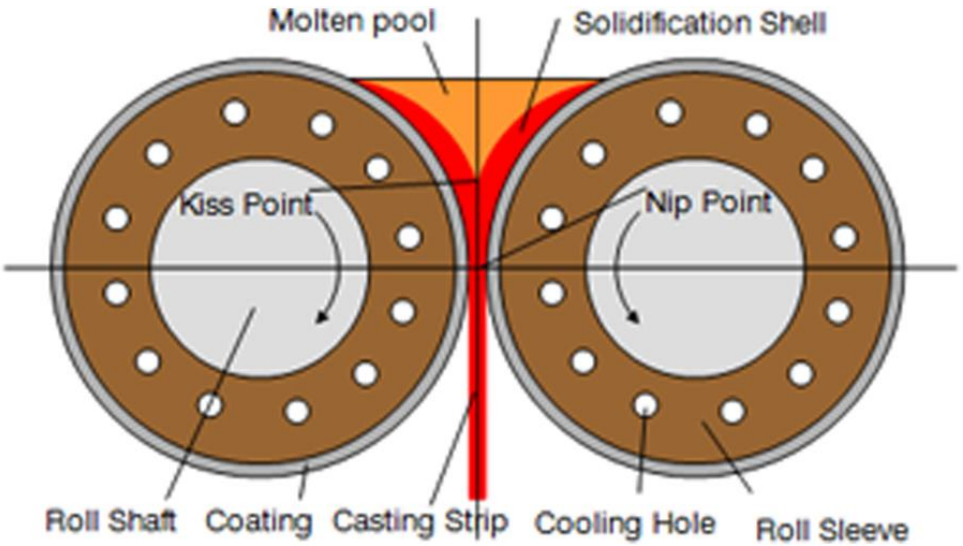
Reactivity of Nd/Di with Oxygen
Reactivity of Nd/Di with crucible
Nd/Pr vaporization

VIM of IPT (capacity: 2-3 kg)

Raw Materials

- High purity Fe
- Fe-B or B
- Di

Fast Cooling – Strip casting

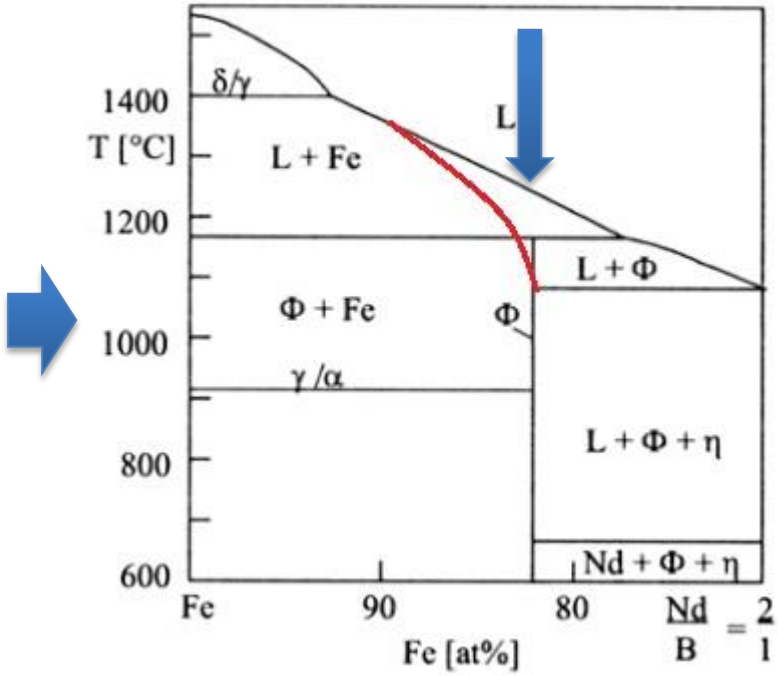


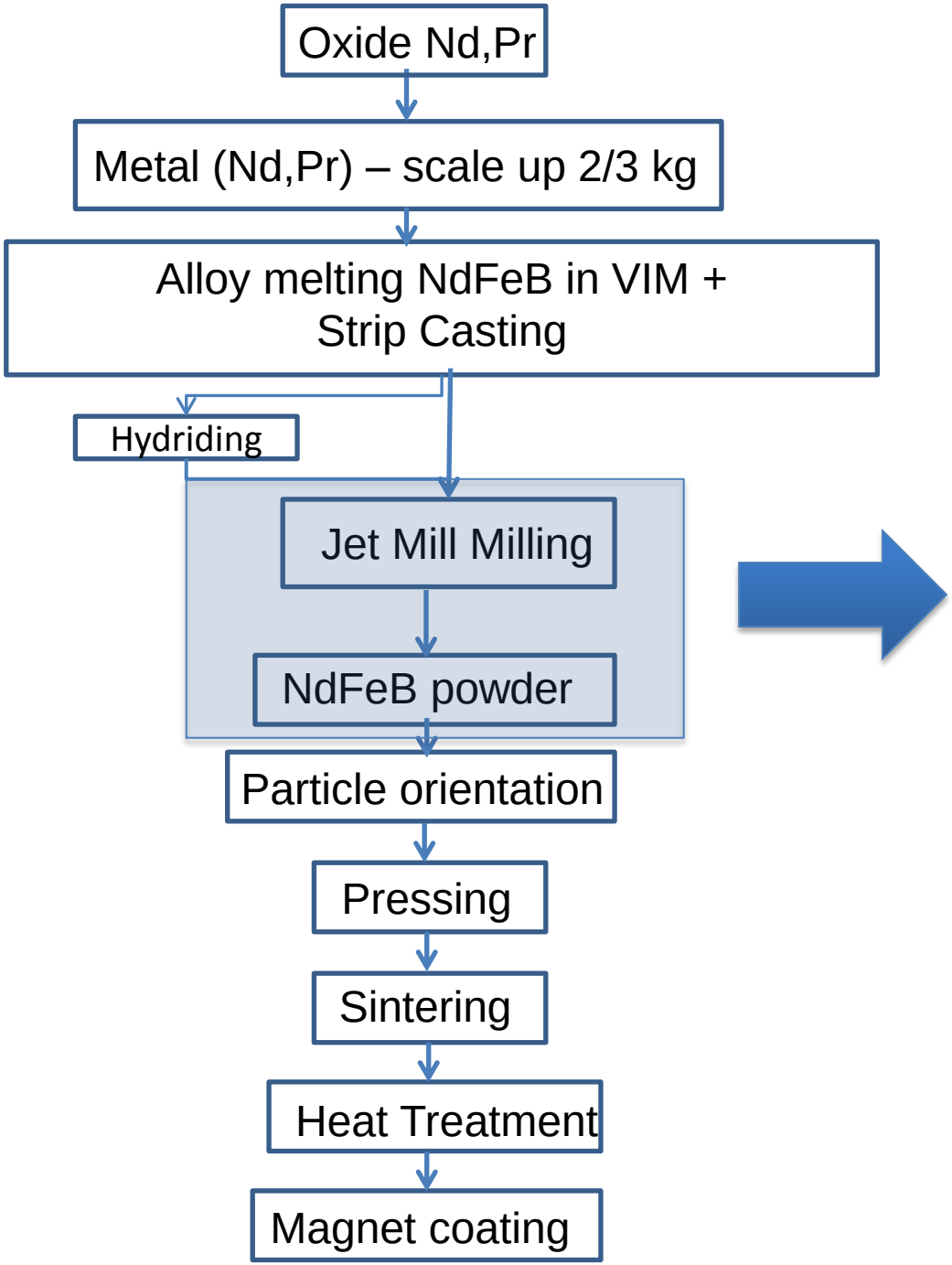
Main Challenges:

- Prevent Fe(α)
- Nd rich phase in grain boundary (η)

(improving hydriding and magnetic properties)

- Columnar grains - 90% width < 25 µm





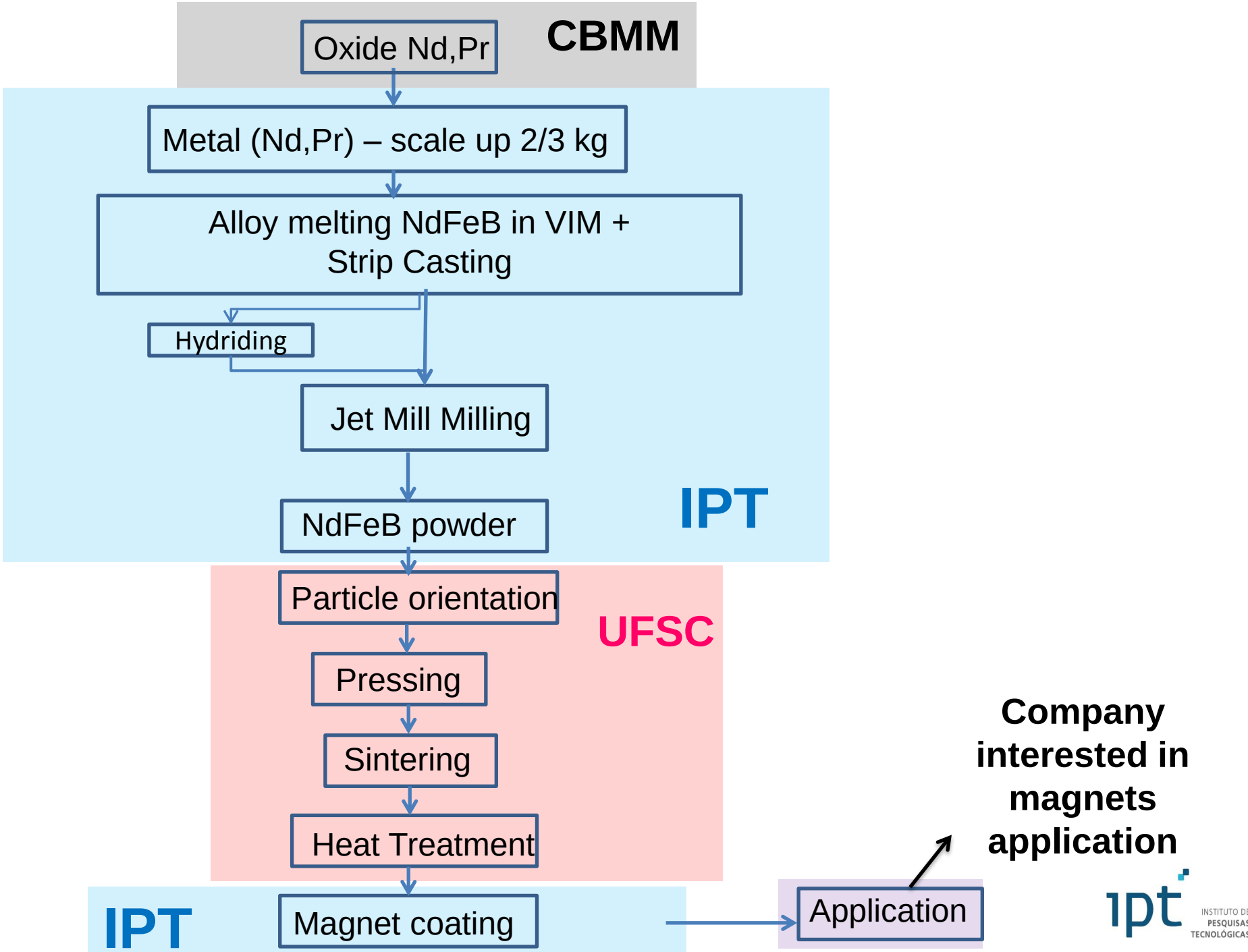
Milling – Jet Mill

- Pre-milling

- Milling - *Jet Mill*

Main Challenges:

- Particle size 2-3 µm
- O < 1000 ppm


CBMM
Oxide Nd,Pr
Metal (Nd,Pr) – scale up 2/3 kg
Alloy melting NdFeB in VIM +
Strip Casting
Hydriding
Jet Mill Milling
NdFeB powder
IPT
Particle orientation
Pressing
Sintering
Heat Treatment
UFSC
IPT
Magnet coating
Application
Company
interested in
magnets
application
ipt
INSTITUTO DE
PESQUISAS
TECNOLÓGICAS

Possibilities of cooperation

Didymium oxide reduction by Electrolysis:

- Identification and quantification of perfluorcarbon gases generated during electrolysis and investigation of routes of gas treatment.
- Determination of didymium (Nd and Pr) oxide solubility and its dissolution kinetic (including a model) in molten fluoride salts (effect of salt chemical composition).
- Possibility of use of inert anode in the dydimium/Neodymium electrolysis.
- Fundamental study of kinetic of (Nd,Pr) oxide reduction

Possibilities of cooperation

(Nd,Pr)-Fe-B alloy and stripcasting:

Effect of cooling rate (wheel speed) of stripcasting and tapping temperature on microstructure of (Nd,Pr)-Fe-B alloys