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Pyrometallurgical Research at SINTEF and NTNU in Norway

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Abstract – The Norwegian Ferro-alloy Industry and the model for research cooperation between SINTEF, NTNU, and the Norwegian ferro-alloy industry is presented as an introduction. The research within pyrometallurgy is illustrated by examples from characterisation of Mn-ores and characterisation of carbon materials. Examples from studies of reaction mechanisms in laboratory- and pilot-scale experiments are presented, in addition to an example of industrial off-gas measurements. Education possibilities at NTNU are also described.

INTRODUCTION

Traditionally, Norwegian industry has been producing ferromanganese and ferrochromium alloys, silicon, and silicon-alloys, in addition to aluminium. Ilmenite smelting and SiC production are also included in pyrometallurgy activities. In addition, there are hydrometallurgical processes such as Zn production and hydrometallurgical-based silicon production, the Silgrain process. In later years, also the production of silicon and silicon wafers to solar cells has led to new industry in Norway. Some of the basic technologies used in today's submerged-arc furnaces were developed in Norway; for example, the Søderberg electrode was developed by the Norwegian company Elkem in cooperation with researchers at NTNU. The ferro-alloy production in Norway includes today silico-manganese, ferromanganese, ferrosilicon and silicon, produced by Elkem, FeSil, Finnfjord, Wacker, Eramet Norway, and Vale Manganese Norway. In 2009, their market share was around 5%, representing approximately 800 000 tons of various Si and ferro-alloys with a value around US $1300 million[1].

All the Norwegian ferro-alloy producers are members of The Norwegian Ferro-alloy Producers Research Organisation, FFF. Here they cooperate about non-competitive, generic research projects, mainly in cooperation with and partly funded through the Norwegian Research Council, and with SINTEF/NTNU as active research partners. Much of this research is open and published. Research in more competitive and confidential subjects is done as direct industrial projects by each industry separately. Funding from the Norwegian Research Council (NRC) is given to the best projects in open competition between R&D projects that meet the project requirements. Projects with cooperation between several industrial partners are preferred.

RESEARCH AT SINTEF / NTNU

SINTEF is the largest independent research organization in Norway, with more than 1700 employees. The Norwegian University of Science and Technology (NTNU) is the largest technical university in Norway. Together, these two organizations are the strongest research environment within material technology, and especially within pyrometallurgical research in Norway. The two institutions cooperate, as illustrated in Figure 1, in a unique model where both laboratories and personnel are shared. SINTEF is responsible for most of the confidential industry projects, while NTNU is responsible for education. Open research is done in both institutions. The cooperation between SINTEF and NTNU in all types of projects gives more available competence and laboratory facilities than work done by each institution alone. Although there is a strong modelling group at SINTEF, the major part of the research carried out is based on experimental work.

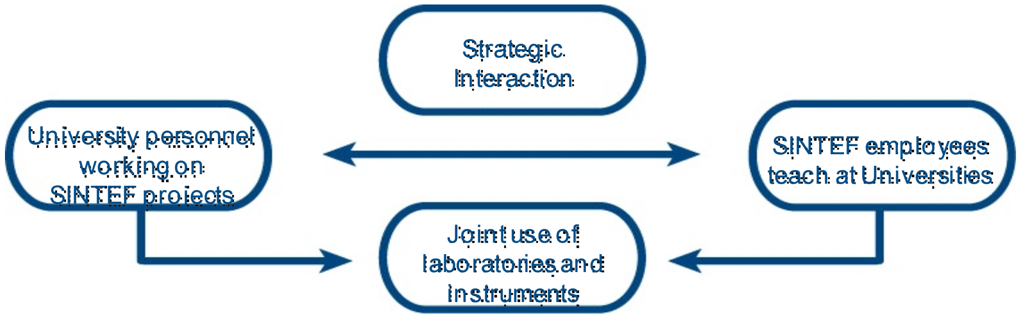


Figure 1: Model for cooperation between SINTEF and NTNU

The most important research areas and equipment within materials technology are shown in Table.

Table I: General overview of equipment and research within materials at SINTEF and NTNU

Type of equipment	Types of research
■ Characterisation ■ Standardised tests ■ Laboratory tests ■ Small-scale tests ■ Pilot-scale tests ■ Industrial measurements	■ Mineralogy ■ Ore dressing ■ Powder technology ■ Ferro-alloy production ■ PV Si production ■ PV Si characterisation ■ Alloy characterisation

As the academic environment has a strong connection to the industry, the main focus in the metallurgical research at NTNU/SINTEF has followed the processes in Norwegian industry. SINTEF/NTNU also does research for non-Norwegian companies. In this paper, some examples on the research in FFF projects within Mn and Si production will be shown. Also, the educational side of materials technology at NTNU will be elaborated on.

MANGANESE ORES

Characterisation of raw materials for the ferro-alloy industry, and interpretation of how the different properties affect furnace performance and product quality are an import part of the research done at SINTEF and NTNU. Much of the work is concentrated on characterisation of Manganese ores.

Performance of industrial FeMn furnaces seems to vary with ore type. The correlation between ore properties and their behaviour in the FeMn processes are investigated in several different projects. Ore properties, such as mineralogy, thermal conductivity, and porosity, are expected to affect properties like CO reactivity, cold- and hot-strength, and melting point properties. Thermal properties are also important for quartz and quartzite raw materials. While some of these properties are discussed in more detail in other papers at this conference[2,3], investigations[4,5,6] of the mineralogy of various manganese ores and their changes during heating are presented here.

Minerals are identified by XRD combined with optical microscopy. In addition, EPMA will provide important information of the mineral chemistry. At NTNU, the Department of Geology and Mineral Resources Engineering have the possibility for quantitative determination of mineralogy by XRD. The mineral identification is done by use of the ICDD database and the BRUKER eva program. After mineral identification, the mineralogy may be quantified by the Rietveld method, using the software package TOPAS4. The fundamental parameter approach used in TOPAS enables the quantification of complex samples like manganese ores[4].

Table II shows the mineralogy of Gabonese ore. During heating in CO gas, the total mineralogy changes, as seen in Table III. The mineralogy will, as discussed in other publications[5,6], depend both on temperature and on gas phase, and varies with composition and mineralogy of the ore type. The differences in mineralogy will, naturally enough, lead to a difference in furnace properties from a lumpy ore to a sinter. But, even more important is that this will change the charge material descending in the furnace and might affect the reactions at the top of the coke bed where the reduction starts.

Table II: Optical appearance and chemistry of phases in Gabonese ore[4]

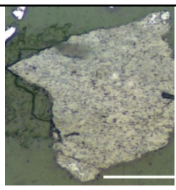
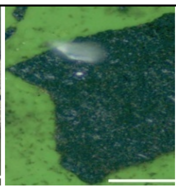
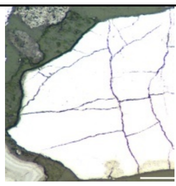
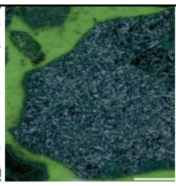
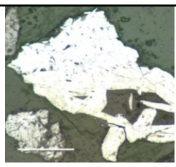
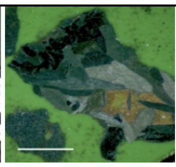
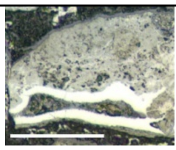
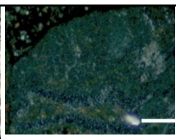
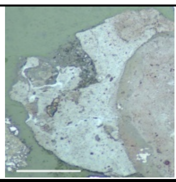
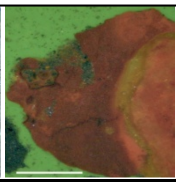
Mineral	Plane polarised	Crossed nicols	Al	O	Si	K	Ba	Na	Mn	Fe
Cryptomelane 35%			1.4 (0.8)	36.4 (1.1)	0.1 (0.0)	1.0 (0.5)	0.2 (0.2)	0.1 (0.0)	57.6 (1.7)	0.6 (0.6)
Nsutite 32.6%			0.4 (0.3)	37.6 (0.5)	0.1 (0.1)	0.2 (0.1)	0.0 (0.0)	0.0 (0.0)	60.1 (1.1)	0.2 (0.1)
Pyrolusite 12%			0.4 (0.3)	35.3 (0.0)	0.2 (0.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	60.0 (0.0)	0.1 (0.0)
Lithiophorite 7%			12.5 (1.3)	42.6 (3.5)	0.6 (0.7)	0.2 (0.2)	0.0 (0.0)	0.0 (0.0)	35.1 (1.6)	1.0 (0.9)
Hematite + Goethite + Lithiophorite mixture			9.6 (3.4)	38.7 (2.5)	6.8 (2.5)	0.3 (0.2)	0.1 (0.0)	0.0 (0.0)	1.2 (1.1)	38.4 (6.5)

Table III: Rietveld quantification of heated Gabonese ore[1]

Conditions	Mineral	Formula	Wt%
800°C, CO	Manganosite	(Mn, Fe)O	76.2
	Galaxite	$(Mn^{2+}, Fe^{2+}, Mg^{2+})(Al, Fe^{3+})_2O_4$	14.4
	Iron alpha	Fe	<1
	Quartz	SiO_2	8.7
	Graphite-3R	C	<1
1200°C, CO	Tephroite	$(Mn, Mg, Fe)_2SiO_4$	24.3
	Manganosite	(Mn, Fe)O	56.3
	Iron alpha	Fe	1.4
	Spinel	$(Mn, Mg, Fe)Al_2O_4$	8.6
	Unidentified		9.4

CARBON SOURCES

As for the manganese ores, knowledge about the properties of carbon sources and an understanding of their effect is a crucial competence for furnace operation. This becomes more and more important with increasing scarcity of good raw materials. For carbon sources, the FeMn producers and the Si producers have different specifications. While the silicon producers need a carbon with high SiO(g) reactivity, the FeMn producers usually look for the cheapest possible carbon source with a certain strength. However, the CO_2 reactivity, slag reactivity, and the electrical resistivity will also affect the furnace operation. At NTNU/SINTEF these properties are measured.

The SINTEF SiO reactivity test was developed by SINTEF researchers J.K. Tuset and O. Raaness in the early 1970s, aiming to rank carbon sources used in the industry with respect to kinetic and equilibrium properties. This can be done by studying the reaction between SiO(g) and C(s) expressed in the following equation:

$$SiO(g) + C = SiC + CO(g) \qquad [1]$$

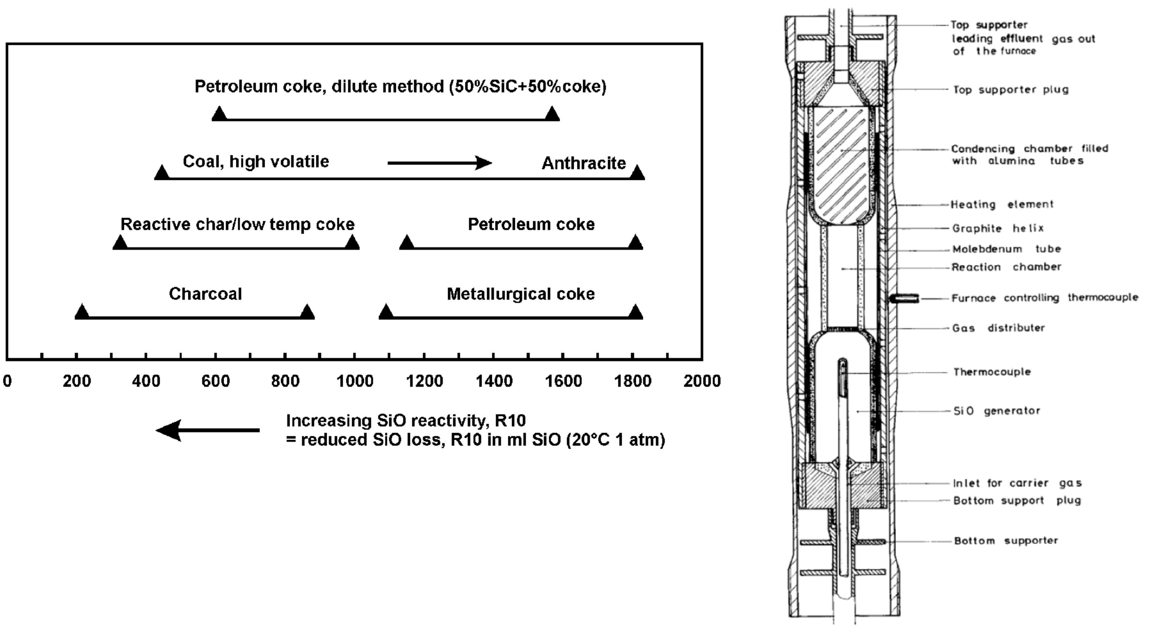


Figure 2: SiO reactivity of various carbon sources and SiO reactor[7,8]

Originally, the test was designed for coke and charcoal, but has later been extended to include other carbon sources. Figure 2 shows the typical reactivity for various carbon sources used in the industry as well as the reactor itself.

Electrical properties for the carbon materials will affect the energy distribution in furnaces. The properties at high temperatures are the most important and also the most difficult to measure. The electrical resistivity of single particles of carbon, of coke-to-coke connections, and of dry coke beds was investigated by P.A. Eidem[9,10] who designed a reactor for such measurements. His investigations showed dramatic differences in the resistivity of various carbon materials, as seen in Figure 3.

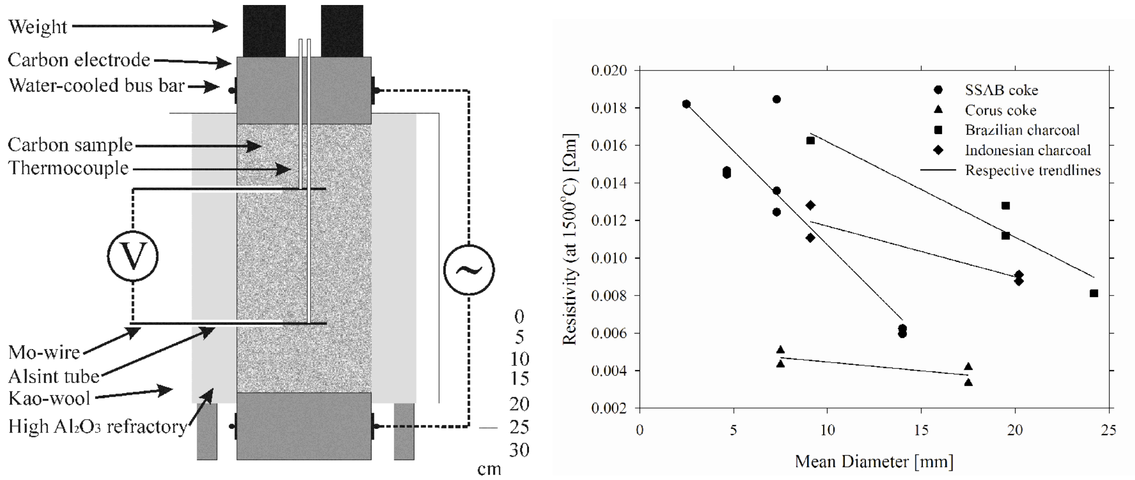


Figure 3: Reactor and some examples of electrical resistivity of dry cokebeds[10]

EXPERIMENTAL INVESTIGATIONS OF REACTION MECHANISMS

In order to determine the effect of various parameters, for instance ore type, on a process, the reaction mechanisms at the given condition must be known. When the reaction mechanism is known, small-scale laboratory experiments may be performed under controlled conditions. However, in many cases the overall reaction mechanisms are not known, and simulations of industrial processes need to be done. Two examples of studies of this at NTNU/SINTEF is the usage of a mid-scale (50 kVA) induction furnace and a one-phase pilot-scale furnace (440 kVA).

The behaviour of different ores on top of the coke bed in a slag process has been investigated in a 50 kVA induction furnace. As the flow of slag through the coke bed is important, it is essential to have industrial-sized materials. Use of a graphite crucible with about 11 cm inner diameter means that the raw materials in the experiment in many cases can be close to industrial-sized materials. The furnace can be set up to give a temperature gradient in the crucible, and this feature can be utilised in experiments where a gradient is needed. Quantification of melting and reduction rate of manganese ores can be investigated in this manner, as shown in Figure 4.

This furnace is also used to simulate the Si operation where the maximum temperature is as high as 2000°C in the bottom of the crucible, and with a temperature gradient to simulate condensation of SiO gas.

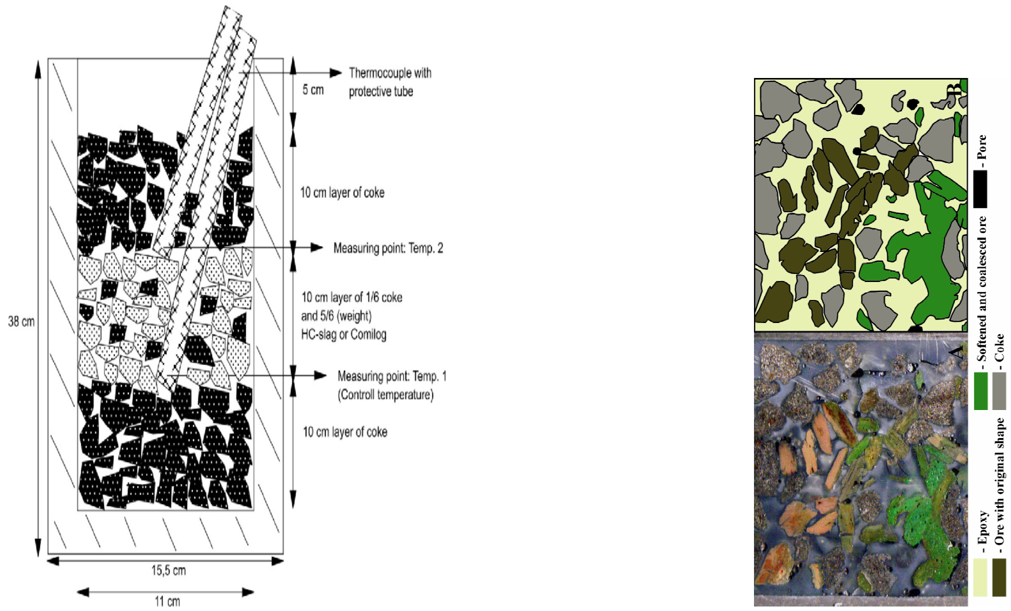


Figure 4: Crucible and charge used in the induction furnace, to investigate how the ore reduces and flows through a cokebed[7]

The experiments above allow studies of selected temperature zones and reactions under given conditions. Studies in an even larger scale are needed, to select out the most important reactions and the temperatures at which they occur. At SINTEF/NTNU, this is done by pilot-scale experiments.

In the 440 kVA pilot-scale furnace, the whole industrial Si- or FeMn-process may be simulated. The furnace is filled with epoxy and dismantled after the experiments. This gives very valuable and, correctly positioned, information about zones and reduction paths. Figure 5 illustrates how the furnace is operated, and shows some results from an experiment with silico-manganese production.

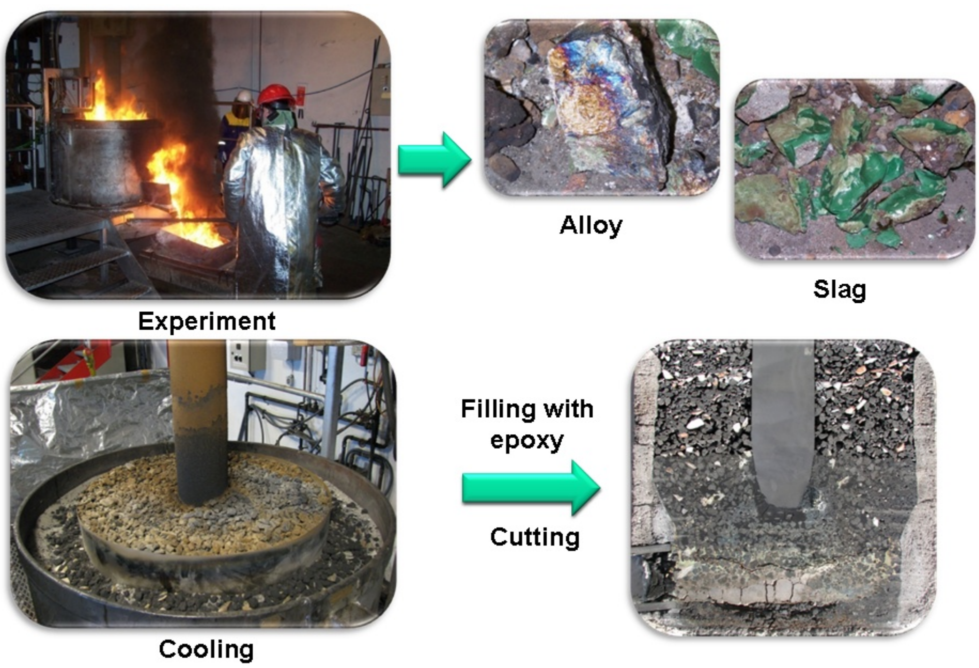


Figure 5: Pictures from the operation of the one-phase pilot-scale furnace[4]

After the experiment, the casted cross-section from the furnace is described and samples are taken out and studied by microscope and EPMA. Figure 6 shows an example from silico-manganese production where MnO was reduced from more than 60% of the charge down to 8–29% at the top of the coke bed. Also, the silicon in the metal is already up to 16% at the top of the coke bed. These kinds of experiments have shown how the major part of the reduction is occurring at the top of the coke bed, as the unreduced slag is too viscous to flow into a coke bed. This also means that the coke size may contribute to the temperature in the coke bed, as the slag flow into the coke bed is dependent on the coke particle size.

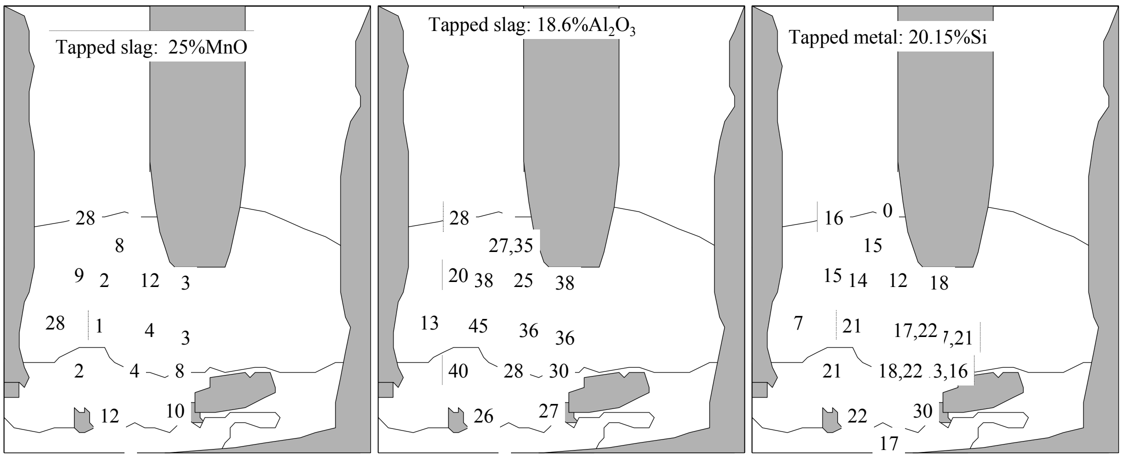


Figure 6: Content of MnO in the slag, Al_2O_3 in the slag, and Si in the metal after a SiMn test[8]

INDUSTRIAL MEASUREMENTS OF OFF-GASES

The Norwegian ferro-alloy and material industry cooperate closely in solving environmental problems and have a long tradition in doing so. Equipment and competence from the group at SINTEF/NTNU working with industrial measurements have been used in these projects. Different types of modern equipment for environmental measurements are available. A combination of emission measurements and registration of process parameters are, in addition, used to gain information about the mechanisms for generation of emissions and by this to find operational parameters and technologies to reduce emissions. Equipment, both for characterization of fumes and exhaust, and for high-temperature measurements is a part of the overall package. The characterisation equipment includes:

- ✓ FTIR Spectrometer
  - – Portable and Open Path
- ✓ Portable mass spectrometer
  - –PAH, dioxin and heavy metals
  - –Temperature range up to 1300°C
- ✓ ELPI on-line particle measuring
  - – High temperature, < 1300°C

– 7 nm – 10 µm measuring range
- ✓ Laser gas, HF, and H_2O measurements
- ✓ Various pyrometers and equipment for temperature measurements

Measurement of dust and gaseous emissions during an avalanche in a silicon furnace[13] is shown in Figure 7. This illustrates the increase in all emissions, including dust, and also a temperature increase, during an avalanche. This is further examined in ongoing projects.

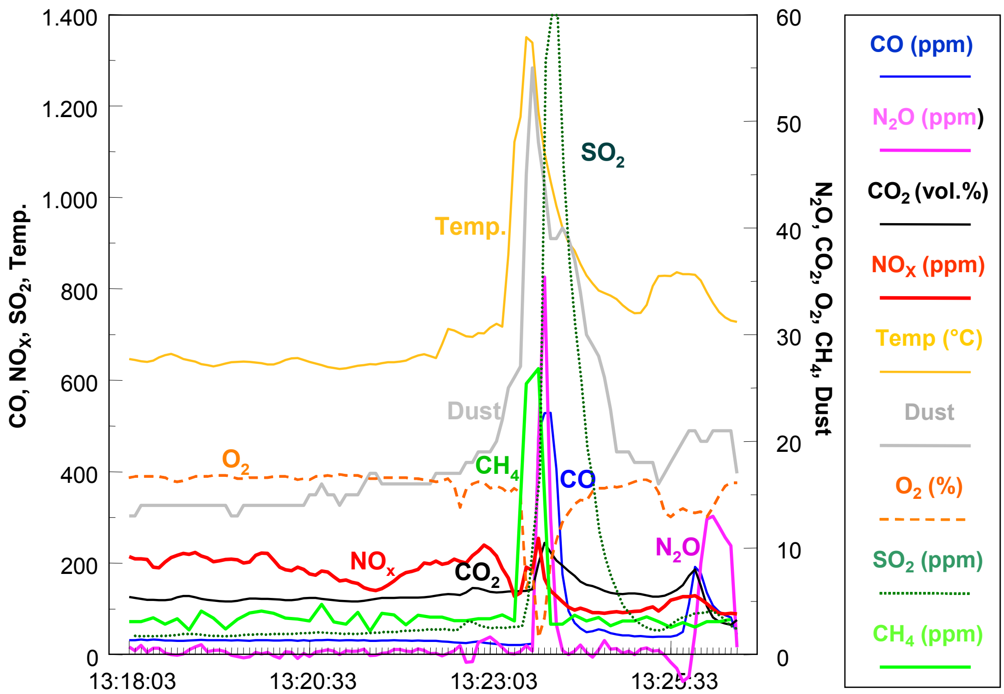


Figure 7: Measurements of off-gas during an avalanche in a silicon furnace

EDUCATION AT NTNU

The basis for the technical part of NTNU is the old German 'Hochschule', where the students take their five-year master degree. This tradition is still the rule at many of the technical education institutions, also for Material Science and Engineering (MSE). Hence, the students do not go for a Bachelor degree first, but go straight to a Master.

In the first 2–3 years, the courses are common for all the students of Material Science and Engineering (MSE). In their fourth year, they can choose between three different directions:

1. Metal production and recycling
2. Materials development and properties
3. Materials for energy technology

For students with a bachelor degree, it is also possible to take the master study, based on the 4th and 5th year at NTNU within material Science and Engineering. There is both a national Master program, but also some more specialized international Master programs, *e.g.* 'Light metals' and 'Ferro-alloy and silicon production'. As there are no tuition fees in Norway, this is also the case for the international Master programs.

Figure 8: Pictures of the main building and the student society at NTNU

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1979 -1990	Engineer in Ore Geology and ore dressing at Rana Gruber, Norwegian Iron Ore Mine
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1993 -1995	Investigation of contaminated soil from Coke plant for Molab
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