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ACTA UNIVERSITATIS OULUENSIS


*Jari Näsi*

# INTENSIFIED USE OF PROCESS MEASUREMENTS IN HYDROMETALLURGICAL ZINC PRODUCTION PROCESSES

*FACULTY OF TECHNOLOGY,*
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# INTENSIFIED USE OF PROCESS MEASUREMENTS IN HYDROMETALLURGICAL ZINC PRODUCTION PROCESSES

Academic dissertation to be presented, with the assent of the Faculty of Technology of the University of Oulu, for public defence in Kuusamonsali (Auditorium YB210), Linnanmaa, on June 8th, 2007, at 12 noon

OULUN YLIOPISTO, OULU 2007

Acta Univ. Oul. C 277, 2007

Supervised by
Professor Kauko Leiviskä

Reviewed by
Doctor Kimmo Konkarikoski
Doctor Björn Saxén

ISBN 978-951-42-8490-8 (Paperback)
ISBN 978-951-42-8491-5 (PDF)
http://herkules.oulu.fi/isbn978951428491 5/
ISSN 0355-3213 (Printed)
ISSN 1796-2226 (Online)
http://herkules.oulu.fi/issn03553213/

Cover design
Raimo Ahonen

OULU UNIVERSITY PRESS
OULU 2007

**Näsi, Jari, Intensified use of process measurements in hydrometallurgical zinc production processes**
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*Acta Univ. Oul. C 277, 2007*
Oulu, Finland

## *Abstract*

This thesis pursues to evidence that it is possible to get information on the behaviour of a complex chemical process by data-based analysis, even though the accurate reaction chemistry is not known.

In the hydrometallurgical zinc production process, metallic zinc is produced by reducing it from aqueous solution. The essential part of the process is the purification of zinc sulphate solution, where all elements nobler than zinc are removed by deposition from the solution. These elements lower the efficiency of the electric current drastically and cause zinc dissolution even in the smallest amounts. Process monitoring supplies a remarkable amount of on-line measurement data and analysis information. This makes it possible to use data-based methods for the evaluation of deposition reactions.

The purpose of this thesis was not to specify reaction equations, but to evaluate which of the known reactions will occur in different process conditions. This was done by diagnosing the purification process of zinc sulphate solution and by combining measurement information with reaction models. An increased understanding of process stability also affects solution purification costs. The results gave new information about the purification process of zinc sulphate solution and its accelerating and decelerating components. The second target was to develop a modular, model-free method of signal validation and estimation, suitable for implementation in the control system in the form of a simple, configurable algorithm. Combining measurements confidence level-based information with fuzzy logic provides a compact system that is easily implemented in the process automation system. The algorithm that was developed was tested in a direct leaching process, where the combination of fast on-line sensors and accurate reference measurement was needed. Measurement data came from an operational zinc plant, so the amount of factory testing was strictly limited. Data evaluation was based on long-term variations in process conditions, possible disturbances and breakdowns of the measurement devices.

*Keywords:* deposition efficiency, optimal estimate, process control, solution purification

**Näsi, Jari, Prosessimittausten käytön tehostaminen ja mittaustiedon tarkentaminen sinkin hydrometallurgisessa valmistamisessa**
Teknillinen tiedekunta, Oulun yliopisto, PL 4000, 90014 Oulun yliopisto,
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*Acta Univ. Oul. C 277, 2007*
Oulu

## *Tiivistelmä*

Tämä väitöskirja pyrkii osoittamaan, että monimutkaisen kemiallisen prosessin toiminnasta voidaan saada tietoa prosessimittauksista laskettujen tunnuslukujen ja niihin vaikuttavien tekijöiden mallintamisen avulla, vaikka reaktioiden tarkkaa kemiaa ei tunneta. Tutkimuskohteena käytetyssä sinkin hydrometallurgisessa valmistuksessa tärkeimpiä osaprosesseja ovat liuotus, haitta-aineiden saostus ja elektrolyyttinen pelkistys. Haitta-aineiden saostaminen tapahtuu reagenssien avulla. Reaktiossa on mukana sekä kiinteä, nestemäinen ja kaasufaasi, joiden välisiä reaktiota ja yhteisvaikutusta ei pystytä tarkasti tutkimaan ja määrittämään. Prosessista on kuitenkin saatavilla huomattava määrä mittaus- ja analyysitietoa, joten eri saostusreaktioihin vaikuttavien tekijöiden vaihtelua voidaan tutkia datapohjaisesti.

Tutkimuksen tarkoituksena oli selvittää, kuinka suurelta osin tunnetut reaktiot toteutuvat ja kuinka suuri on se osuus reaktioista, joita ei pystytä selittämään. Lisäksi eri luotettavuusasteisen mittaustiedon yhdistämisellä pyrittiin lisäämään mittaustiedon luotettavuutta ja tuottamaan operaattoreille entistä käyttökelpoisempaa informaatiota prosessin tilasta. Tätä varten kehitettiin helposti käyttökohteen mukaan adaptoitava laskenta-algoritmi, joka tuottaa mittaustietoihin perustuvan estimaatin. Estimaatin toimintaa testattiin suoraliuotusprosessissa, josta oli saatavilla sekä on-line mittauksia että tarkkoja referenssimittauksia.

Tutkimusaineistona käytettiin Kokkolan sinkkitehtaalta saatavaa mittausdataa. Mittausaineisto työhön on suurimmaksi osaksi peräisin toimivasta tehdasprosessista, joten tuotannolliset seikat ovat voimakkaasti rajoittaneet prosessikokeiden tekoa. Työssä onkin turvauduttu pitkällä aikavälillä tapahtuneiden muutosten sekä mahdollisten prosessihäiriöiden ja analysaattorien vikaantumisten aiheuttamien muutosten analysointiin. Tilastollisen analysoinnin avulla selvitettiin, tapahtuuko prosessiparametrien välisissä riippuvuuksissa muutoksia eri mittausaineistojen välillä.

Tutkimustulosten perusteella pystytään pitämään saostusprosessi paremmin optimaalisella toiminta-alueella. Kehitetty "optimaalisen estimaatin" laskenta-algoritmi on asennettu toimimaan tehtaan prosessinohjaustietokantaan.

*Asiasanat:* liuospuhdistus, optimaalinen estimaatti, saostustehokkuus

# Acknowledgements

The research work reported in this thesis was carried out at the University of Oulu in the Control Engineering Laboratory during the years 2001–2007. I wish to express my gratitude to my colleagues who have supported me during the work. In particular, I would like to thank my supervisor, Professor Kauko Leiviskä, for his guidance during the research and writing process.

I am most grateful to the reviewers of this thesis Doctor Björn Saxén from Outotec Research Oy and Doctor Kimmo Konkarikoski from Tampere University of Technology for their comments on the thesis.

I would like to thank my colleagues and friends at the Control Engineering laboratory and Geological Department. Special thanks to Docent Kari Strand, who offered me the opportunity to familiarize myself with the career of research scientist and to my colleague Aki Sorsa for teamwork in the research projects and writing of conference papers. I also wish to thank Mika Ruusunen and Ari Isokangas for the many useful discussions related both to the research work and everyday problems.

The research projects were financed for the most part by TEKES and Outotec Research Oy, for which I am most grateful. I would also like to thank the Outokumpu Oyj Foundation, Tauno Tönning Foundation, Technological Foundation and Finnish Society of Automation for their valuable support during my research and writing work.

Finally I thank my family, parents and friends, who have encouraged and supported me during these past years.

Oulu, May 2007 Jari Näsi

# List of abbreviations

| | |
|---|---|
| Ag | Silver |
| $As_2O_3$ | Arsenic trioxide |
| C | Carbon |
| Cd | Cadmium |
| CO | Carbon monoxide |
| $CO_2$ | Carbon dioxide |
| Co | Cobalt |
| Cr | Chromium |
| Cu | Copper |
| EWMA | Exponentially weighted moving average |
| FDI | Fault detection and isolation |
| FeOOH | Ferrihydrite |
| $FeS_2$ | Pyrite |
| Ge | Germanium |
| $H_2O$ | Water |
| $H_2SO_4$ | Sulphuric acid |
| Hg | Mercury |
| In | Indium |
| $MnO_2$ | Manganese dioxide |
| MV | Measurement value |
| NaCl | Sodium chloride |
| NaOH | Sodium hydroxide |
| Ni | Nickel |
| $O_2$ | Oxygen |
| PF | Particle filter |
| Pb | Lead |
| $PbSO_4$ | Lead sulphate |
| S | Sulphur |
| $Sb_2O_3$ | Antimony trioxide |
| Se | Selenium |
| SEVA | Self-validating sensor |
| $SO_2$ | Sulphur dioxide |
| SPC | Statistical process control |
| Ti | Titanium |
| V | Vanadium |

| | |
|---|---|
| VMV | Validated measurement value |
| VU | Validated uncertainty |
| Zn | Zinc |
| ZnO | Zinc oxide |
| $ZnO \cdot Fe_2O_3$ | Zinc ferrite |
| ZnS | Zinc sulphide |
| $ZnSO_4$ | Zinc sulphate |
| σ | Sigma or the standard deviation |

# List of original papers

I Näsi J (2003) Statistical analysis of cobalt removal from zinc electrolyte using the arsenic activated process. Journal of Hydrometallurgy 73: 123-132.

II Näsi J & Leiviskä K (2005) Solution filtration in cobalt removal process; detection of varying process conditions. Minerals Engineering 18(13-14): 1253-1258.

III Näsi J & Sorsa A (2006) Confidence Level Based Optimal estimation of on-line measurement. ISRA 2006, August 25-28. Hidalgo, Mexico, 331-336.

IV Näsi J & Sorsa A (2005) Confidence based estimation and deterioration indication of on-line measurement. ICINCO 2005, September 14-17. Barcelona, Spain, 340-344.

V Näsi J, Sorsa A & Leiviskä K (2005) Sensor Validation and Outlier Detection Using Fuzzy Limits. CDC-EEC'05, December 12-15. Seville, Spain, 7828-7833.

# Contents

# 1 Introduction

Measurements are the key to valid process control in the process industry, where the effectiveness of production and profitability are closely related to the quality of the product, and where quality again depends on process control and hence on measurements. The reliability and performance of complex production systems depend largely on the accuracy and reliability of measurements while the economic efficiency of production relies on the effective use of measurements. The process industry makes use of both on-line measurements and laboratory analyses to monitor and control processes. This kind of backup system helps the operator to make his decisions by combining data from several measuring devices.

## 1.1 Research problem

In our modern competitive society, intensified production, with high-level products and low working costs, is in a central position. The approach applied in this thesis is therefore easily justified – it aims at improving the usefulness of the available data without new investment costs.

This thesis pursues to *evidence that it is possible to get information on the behaviour of a complex chemical process through data-based analysis even though the accurate reaction chemistry is not known.* Increased understanding of process stability also affects factors such as solution purification costs. The main purpose here was to develop methods for diagnosing the purification process of zinc-sulphate solution and its accelerating and decelerating components. This was done by combining measurement information with reaction models.

In the process industry, the situation is repeatedly encountered where the same process variable (usually a quality variable) is measured both on-line as well as being analysed in the laboratory. The optimal use of this redundant information is a crucial question for process control. The second target of the thesis was to *develop a signal validation and estimation algorithm which would be modular, model-free and suitable for implementation in a control system in a configurable form.* Many of the existing techniques in the literature naturally require some form of sensor (and possibly plant) model, which in this application is replaced by data-based reasoning. In validating on-line measurement by laboratory analysis, used in this thesis, less frequently updated but more accurate information is used to validate frequently updated but less accurate on-line

measurements. The methods consist of the calculation of confidence levels followed by data fusion where both signals are exploited.

## 1.2 Origin of data

This study utilizes data-based analysis. Process data for the research work came from the Boliden Kokkola hydrometallurgical zinc production plant. Pilot plant tests occurred when the batch purification process was replaced with a new continuous purification process (measurement data was available from both pilot- and industrial-scale processes). In the development of the confidence level-based approach, the data for evaluation for the developed algorithm came from the direct leaching process, where both on-line process measurement data and reference analysis were available.

## 1.3 Background to the research

The research activities during the period 2001-2005 and their respective results led to published results and this thesis. The results are part of two large research projects and although the scope of these projects might seem large, these projects provided insights into different aspects of the hydrometallurgical production of zinc and to the evaluation of process measurements.

I would like to point out that in the first article I am the only author and in the rest of the publications I am the primary author. My own contribution to this work, even though research projects were carried out with a larger number of researchers, lies in the process analytical part, statistics and knowledge of chemistry. The tools presented in the case studies, have been developed either by myself or with my colleague Aki Sorsa, who provided excellent use of Matlab on the research projects.

The research projects were:

PRODYNA - Process Dynamics in Tuning Adaptive Intelligent Process Control. Taking place during 2001-2003, the aim was to develop reliable control systems to improve process control. The project was funded by Tekes (Finnish Funding Agency for Technology and Innovation) and participating companies and it was a part of the technology program Intelligent Automation Systems. The objective in this subproject was to model the cobalt removal stage in hydrometallurgical zinc production. Outokumpu Zinc at Kokkola was replacing the batch process and starting to use the continuous cobalt removal process.

Cobalt removal is the middle step of three-stage solution purification, where copper is removed in the first one and cadmium in the last one. Cobalt removal itself involves four reactors. This project took advantage of intensive data collecting, which was done during the pilot stage. Emphasis was therefore placed on collecting knowledge from solution purification and combining process data with chemical reaction models. Calculation of deposition efficiencies were used to create numerical values for evaluating the success of the deposition process and the effect of the reagents used (Paper 1). In the solution filtration part, the purpose of the work was to compare varying process conditions and to find the correlations between the process parameters and the filter pumping pressures in different circumstances (Paper 2). The results of this part support the first hypothesis.

PRO-ELE – Intelligent analyzers and control in the process and electronics industry. The project was funded by Tekes and participating companies. Taking place during 2003-2005, the project was divided into three subprojects, of which the part discussed in this thesis concentrated on improving controllability in the direct leaching process. In order to achieve the target, a calculation algorithm, called "calculation of optimal estimate", was created. The method combines data from continuous (on-line) measurements from the process and data from (off-line) laboratory analyses based on samples taken from the process. In the calculation, the effects of outliers, bias, and sensor malfunctions are removed, while the accuracy of off-line measurements and temporal dynamics of on-line sensory data is preserved. The purpose was to create an implemented application with an appropriate user interface, which produces the "optimal estimate" from the available signals and is transferable to similar applications after light configuration. The practical implementation for the development stage was done in 2004 and since then it has been in use at Outokumpu Zinc in Kokkola (now Boliden Kokkola). The development stages of the algorithm are reported in three refereed conference papers (Papers 3-5). The results from this part support the second hypothesis.

## 1.4 Research hypothesis

In the case of nonlinear deposition process data, containing varying process delays, the growth in the amount of available data gives a new opportunity to evaluate reasons for process variation and changes. As a consequence, the process technical aim of the work was to find deposition mechanisms that affect the

cobalt removal process, study the behaviour of filtration pressure in good and problematic process conditions and determine the factors that have an effect over a longer time scale.

The research problem as defined above leads to the following two hypotheses, which are the basis for the research.

***Basic statistical methods give appropriate tools for process analysis when combined with a knowledge of chemistry, reaction mechanisms, and dynamics of the process under study.*** Their use is, however, limited to off-line analysis. The on-line use of redundant measurement information requires more efficient signal processing tools.

***Combining a confidence level-based approach with fuzzy logic provides a compact algorithm that can be used to calculate useful estimates and is implementable in the process automation system.***

The hypotheses are tested in a hydrometallurgical process, but the methods as such do not depend on the process.

## 1.5 Progress of the dissertation

During the first years, the writing of the thesis concentrated mainly on the processing of conference papers and articles and during the last year, writing the overview and conclusions. This work has proceeded in parallel with the research projects. The possibility of publishing the achieved results in the form of conference papers and articles encouraged me to collect and report the research results and background theory as well as possible. On the other hand, proper and comprehensive background work during the research project assisted the further writing of the thesis.

The research results were published in the first instance as large and comprehensively as possible in the report series of the Control Engineering laboratory and in the second stage condensed for publication in papers and conferences in this field of research. Altogether, research work on process measurements in hydrometallurgical zinc production processes produced 4 reports in the Control Engineering laboratory series, 4 conference papers and 2 journal articles. All 10 publications are listed below in the order in which they were published. Five of them are included in this thesis, as shown in the part “Original papers”.

- Näsi J (2002) Jatkuvatoimisen liuospuhdistuksen pilot-prosessin mallinnus ja prosessikehitys. Oulun yliopisto, Säätötekniikan laboratorio, Raportti B No 36.
- Näsi J (2002) Adaptive modelling with linguistic equation in process development phase. Case study: Co removal process at Outokumpu Kokkola Zinc Plant. SIMS 2002, September 26–27. Oulu, Finland, 205–209.
- Näsi J (2003) Hydrometallurgisen prosessin tutkimuskohteita osa 1: Suodinpuristimien tukkeentumiseen vaikuttavat tekijät, Oulun yliopisto, Säätötekniikan laboratorio, Raportti B No 43.
- Näsi J & Niemelä P (2003) Hydrometallurgisen prosessin tutkimuskohteita osa 2: Raman analytiikan käyttömahdollisuudet. Oulun yliopisto, Säätötekniikan laboratorio, Raportti B No 44.
- Näsi J (2003) Statistical analysis of cobalt removal from zinc electrolyte using the arsenic activated process. Journal of Hydrometallurgy 73: 123-132.
- Näsi J & Sorsa A (2004) On-line measurement validation through confidence level based optimal estimation of a process variable. University of Oulu, Control Engineering laboratory, Report A No 25.
- Näsi J & Sorsa A (2005) Confidence based estimation and deterioration indication of on-line measurement. ICINCO 2005, September 14-17. Barcelona, Spain, 340-344.
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- Näsi J & Sorsa A (2006) Confidence Level Based Optimal Estimation of On-line Measurement. ISRA 2006, August 25-28. Hidalgo, Mexico, 331-336.

## 1.6 Outline

The first chapter of this thesis describes the problem under investigation, states the hypotheses, presents the research environment and the progress of the dissertation with published papers. The history of the hydrometallurgical production of zinc, process development in the last decades and especially economic and environmental aspects are discussed in the second chapter. The

third chapter evaluates process data, the statistical methods used, signal validation methods and uncertainty of measurements/different sensors. Short descriptions of the papers presented are collected in chapter four. Finally, the most important results from the solution purification and estimation algorithm are summarized and evaluated in the fifth chapter.

# 2 Hydrometallurgical production of zinc

Zinc forms an adherent layer on the surface of iron objects and considerably prolongs the lifespan of steel constructions. In this way, it saves energy and other natural resources like nickel, chromium and molybdenum, which would be the alternative choices as alloying materials in steel.

## 2.1 Short history

Although zinc was first smelted over 1000 years ago in China and India, sophisticated technology for zinc production was first developed in the western civilization in the 18$^{th}$ century (Bond, 1999). The metal produced was called Indian tin or calamine (this term is now reserved for natural zinc carbonate). Two major manufacturing processes have emerged since then. The first is a thermal process where, initially, zinc sulphide ore is roasted in air to produce zinc oxide (ZnO). ZnO is then reduced with carbon at high temperatures and the resultant metal vapours condense into solid metal (Bond, 1999). The reduction of zinc in this process can be summarised as:

$$ZnO\ (solid) + C\ (solid) \rightarrow Zn\ (metal) + CO\ (gas) \quad (1)$$

Unfortunately, this type of zinc production has its drawbacks. The zinc produced is only about 98% pure and the reduction process produces large amounts of harmful greenhouse gases.

The second process is electrolytic where, initially, zinc ore is first roasted at high temperatures and then dissolved into sulphuric solution. In the last stage the zinc ions ($Zn^{2+}$) are electrolysed to metallic zinc at a cathode (Bond, 1999). The overall reaction for the electrolytic production of zinc in the electrowinning process is:

$$Zn^{2+}\ (solution) + 2e^{-} \rightarrow Zn\ (metal) \quad (2)$$

Hydrometallurgy has a much shorter history than production of zinc by smelting, and it can be traced back to the end of the 19$^{th}$ century, when the cyanidation process of gold and silver extraction was invented. The electrodeposition of zinc on iron and steel for protection against corrosion was proposed for the first time in 1840. The First World War (1914–1918) created a demand for zinc for the manufacture of cartridge brass. Zinc for this purpose was obtained by the distillation of commercially available metal. This situation inspired industry in

North America to supply additional metal from ores that were not suitable for standard methods. In British Columbia and Montana, the processes for producing electrolytic zinc and the leaching of a large tonnage of ZnO by sulphuric acid ($H_2SO_4$) were introduced (Habashi, 2005). The roasting – leaching – electrowinning process (discussed in detail in the following chapters) was developed and taken into common use (Fig.2).

In the 1950s, pressure hydrometallurgy was introduced for leaching sulphide concentrates as well as for the direct precipitation of metals from solution. In the 1970s the pressure leaching of zinc sulphide concentrates was applied industrially in Canada. The new process turned the production of zinc into a fully hydrometallurgical process (Fig. 2), thus displacing the roasting of zinc sulphide (ZnS), reduction of ZnO by carbon, and distillation refining of metallic zinc (Fig. 1). The process also freed the zinc industry from the mandatory sulphuric acid production (Habashi, 2005).

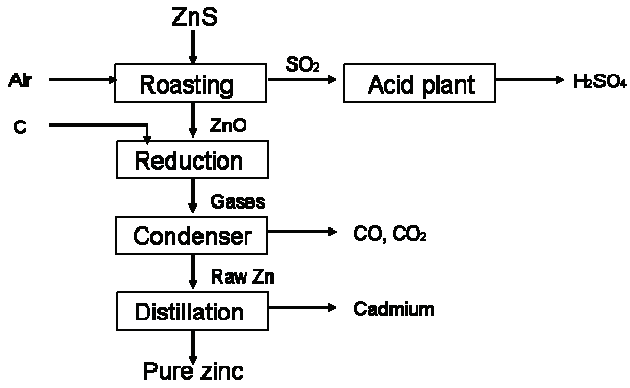


**Fig. 1. The pyrometallurgical process for zinc reduction (Habashi, 2005).**

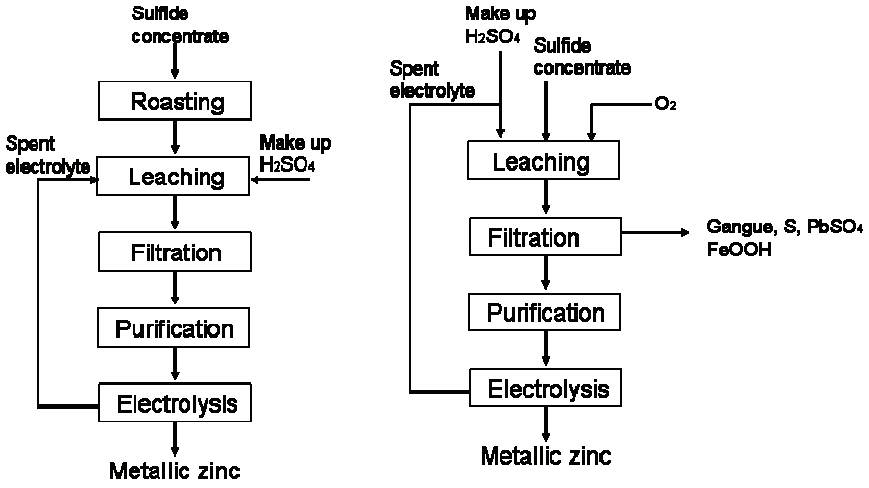


**Fig. 2. The hydrometallurgical processes for zinc production (Habashi, 2005).**

## 2.2 Roasting

Roasting of zinc sulphide concentrate converts sulphides to more useful acid soluble oxides and utilizes the $SO_2$ gas for sulphuric acid production. Roasting is carried out at temperatures around 900-950 °C. The main components of the roasting process are a furnace, waste heat boiler, cyclone, electrostatic precipitator, mercury (Hg) removal and sulphuric acid plant (Nyberg, 2004).

$$2ZnS\ (solid) + 3O_2\ (gas) \rightarrow 2ZnO\ (solid) + 2SO_2\ (gas) \quad (3)$$

Zinc concentration is typically about 55%, with up to 10% iron often being present, together with a number of significantly varying concentrations of minor compounds of e.g. copper, cadmium and lead (Bond, 1999). During the roasting process most of the iron present in the concentrate combines with zinc oxide and forms zinc ferrite, ($ZnO{\cdot}Fe_2O_3$).

In process development, more measurements, analyses and calculated variables have been added to give additional information on the state of the furnace. New control variables have been introduced, like the on-line calculated oxygen coefficient and particle size distribution analysis of the furnace calcine. These will give operators more opportunities to set the process conditions so that they are optimized for the actual concentrate feed mixture (Nyberg, 2004).

## 2.3 Leaching and iron removal

Leaching the calcine in sulphuric acid solution to produce a zinc sulphate solution typically has two stages (normal and high temperature leaching). Normal leaching involves the dissolution of zinc oxide with the sulphuric acid (spent electrolyte) generated from the cell room. This process is also known as neutralization as the acid is neutralized by zinc oxide to form zinc sulphate and water. The high temperature leaching stage involves the dissolution of zinc ferrite with the precipitation of ferric sulphate (Ismael & Carvalho, 2003, Swarnkar *et al.* 1996).
The direct leaching process uses concentrate (without roasting) together with slurry from the conversion process, acid and oxygen. Oxygen, fed to the reactors, is an essential oxidising element in the dissolution of sulphuric concentrates (Kaskiala, 2002).

Zinc sulphate solution obtained by high temperature leaching contains a high level of iron and successful recycling of this solution into the main stream requires a method where the majority of the iron is precipitated as an easily filterable compound. The hydrolyzed ferric ion acts as a metal ion collector and partially removes arsenic, antimony and germanium. Iron is usually removed from leaching solutions by precipitation as goethite, hematite or jarosite. In most of the existing electrolytic zinc plants, the method for iron removal is precipitation as jarosite. The fourth process, known as the "Conversion Process", developed by Outokumpu, Finland, achieves simultaneous ferrite dissolution and precipitation of iron as jarosite in a single step (Swarnkar *et al.* 1996).

A competing method for extracting zinc from zinc ferrites is to leach it with a strong alkaline solution. In direct alkaline leaching, the ferrite structure is broken by fusing the ferrite with sodium hydroxide (NaOH). According to the literature, very little zinc can be extracted at heating temperatures below the melting point of sodium hydroxide (318 °C). At higher temperatures (around 350 °C), the efficiency of zinc extraction increases to around 70%. Recovery can be increased further by washing the solid with water or sodium hydroxide solution. Zinc is recovered from the alkaline leaching solution using electrowinning (Youcai & Stanforth, 2000).

### *2.3.1 Processing of leaching residue*

Recent process development in the leaching process has concentrated on environmental aspects (diminishing the amount of environmentally hazardous

wastes and further processing of by-products). The major environmental problem originating from the zinc electrolytic process is the disposal of iron residues coming from the leaching and purification stages. The large amounts of residue produced by zinc hydrometallurgy are at present stockpiled in various types of impoundments close to the electrolytic plants.

The leaching and iron removal process has economic disadvantages, due to the high cost of impounding jarosite in controlled ponds. Residue, which is contaminated with sulphuric compounds (heavy metals such as Zn, Se, In and Ge), will cause environmental problems in atmospheric conditions. To avoid these problems it is possible to remove iron from the residue as marketable iron products; for example pure hematite that can be used as a pigment or raw material in the steel-making industry. Various approaches for iron recovery have been tested and reviewed in literature (Ismael & Carvalho, 2002).

One example of small-scale recycling is carried out in the Sardinia zinc plant where recovery of valuable elements was investigated. The residue was mixed with raw materials, melted and then crystallized using suitable thermal treatments to obtain glass-ceramic products (Pelino *et al.* 1996).

In some plants (e.g., Cinkur, Kayseri, Turkey), the zinc leach residue is stockpiled for the future recovery of lead. These residues are considered as hazardous wastes due to their significant zinc, lead, and cadmium content. To avoid these problems, the recovery of valuable metals from zinc normal leach residue has been studied and several methods have been implemented:

- Lead and zinc recovery from zinc leach residue by extra roasting, water leaching and NaCl leaching (Turan *et al.* 2004).
- Lead recovery from zinc leach residue by flotation (Rashchi *et al.* 2005).
- Recovery of lead and highly pure silver concentrate from zinc lead residue by a froth flotation process followed by roast-leach-precipitation-reduction (Raghavan *et al.* 1998).

## 2.4 Solution purification

The function of zinc solution purification is to remove elements which would reduce the efficiency of the electrodeposition process. Neutral zinc sulphate solution contains a number of harmful elements, termed impurities. Their impact can be classified as follows:

- Co-depositing with zinc in electrolytic deposition and decreasing the purity of metallic zinc.
- Decreasing the current efficiency (% of the current used which produces zinc) and hence increasing power consumption.

Current efficiency is normally around 94% (Bond, 1999). For example, impurities like antimony and germanium catalyse the competing reaction of hydrogen ion reduction, and decrease the current efficiency (and the process efficiency). The impact of single element impurity concentrations on current efficiency is shown in Fig. 3. When impurities are combined, synergistic effects have even more dramatic consequences on the current efficiency.

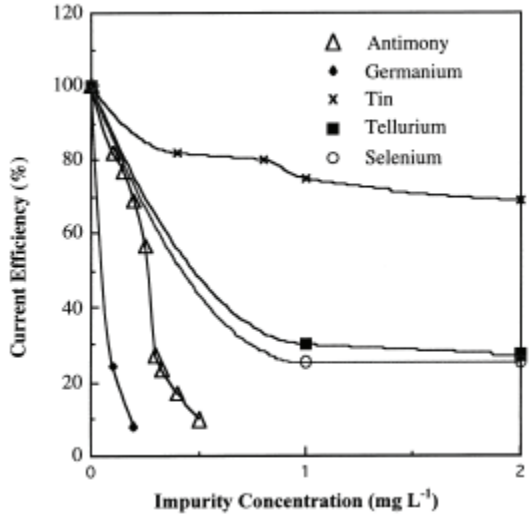


**Fig. 3. The effect of impurity concentration on current efficiency for l-hour zinc electrodeposition from industrial acidic zinc sulphate electrolytes (Mackinnon *et al.* 1987).**

Much work has been done on the purification of raw zinc sulphate solution and different processes have been developed. All systems basically consist of the cementation of impurities with zinc dust. Theoretically one would expect metals to be removed in the order of their electrode potential: Ag > Cu > Pb > Ni > Co > Cd.

Purification of other leaching reactants, such as ammonia, nitric acid, and caustic soda chlorides also requires removal of impurities before electrowinning

(Moghaddam *et al.* 2006, Casaroli *et al.* 2005). In these applications the aim of cementation is similarly to reduce the concentration of impurities to low levels (<1 mg/l) both to enable the production of high quality zinc deposits, and to improve current efficiency during electrowinning.

The best way to deal with impurities is to push process standards continually towards lower concentrations. Elements and their harmful effects are listed in Table 1:

**Table 1. Elements removed during the solution purification and their impact on zinc electrowinning (Bond, 1999)**

| Element | Effect |
|---|---|
| Nickel | can cause holes in deposited zinc when other impurities are present |
| Cobalt | decreases current efficiency in electrolysis when other impurities are present |
| Copper | decreases current efficiency |
| Cadmium | contaminates the final zinc product |
| Arsenic | decreases current efficiency in electrolysis |
| Antimony | in small concentrations (less than 50 ppb) may be beneficial, in greater concentrations decreases current efficiency drastically |
| Manganese | deposits as $MnO_2$ on the lead anode but mainly has an effect on the distribution of other impurities |
| Germanium | even at very low concentrations severely decreases current efficiency in electrolysis |

Solution purification is carried out by zinc dust precipitation over two or three stages (depending on the specified process equipment and reagents used). The classical electrochemical metal displacement reaction, in which metal ions electropositive to zinc are reduced, and the zinc metal is oxidized, is written for example:

$$Zn\ (metal) + Co^{2+}\ (solution) \rightarrow Co\ (metal) + Zn^{2+}\ (solution) \quad (4)$$

In practice, the reactions are more complex and reagents and catalysts are needed to enable the deposition reactions (Paper 1 discusses the deposition process of the impurities more). Two different reagents can be used to deposit impurities like cobalt and nickel. Either arsenic trioxide ($As_2O_3$) or antimony trioxide ($Sb_2O_3$) with zinc dust and leftover copper creates conditions where deposition can occur economically and quickly enough (Fig. 4).

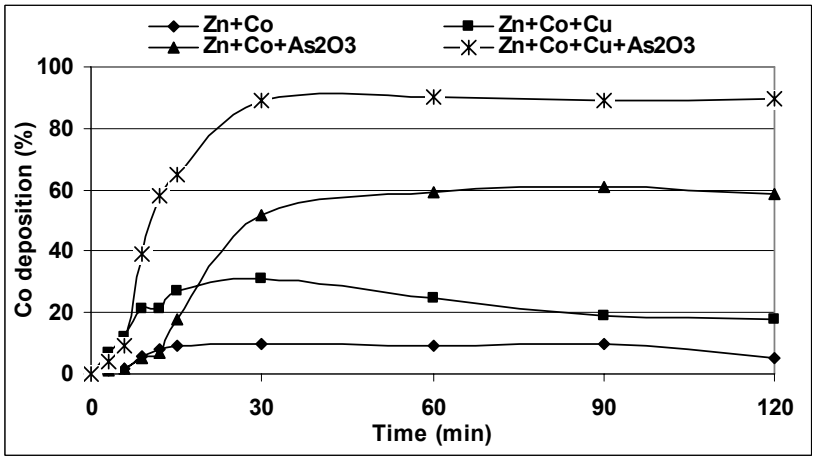


**Fig. 4. Cobalt deposition from zinc sulphate solution. (Ohgai *et al.* 1998)**

### *1.1.2 Reaction kinetics*

Several studies have proved that the reaction path of cobalt cementation cannot be estimated thermodynamically from potential differences between cobalt and zinc but from the presence of mixed cobalt and zinc phases observed in cementation products (Ohgai *et al.* 1998).

The number of purification stages and the use of reagents depend upon the concentration of copper, cadmium, nickel and cobalt present in solution. Removal of copper and cadmium is simple because a small excess above the stoichiometric quantity of zinc dust can remove all the copper and cadmium present in solution (Safarzadeh *et al.* 2007). Most of the raw zinc sulphate solutions contain 10-50 mg/l of cobalt and 10-30 mg/l of nickel. Reagents, like $As_20_3$ or $Sb_20_3$, are used to catalyse the precipitation reaction.

Of the metals which can be deposited electrochemically from aqueous solutions, only iron group metals (Ti, V, Cr, Mn, Co, Ni) begin to deposit on cathodes at potentials which are several tenths of volts smaller than their equilibrium potentials. Other important process impurities, such as Cu and Cd, are deposited close to their equilibrium potentials. This difference in metal deposition causes problems in purification and use of different reagents (Ohgai *et al.* 1998). Deposition has several alternative mechanisms e.g. the formation of an intermetallic compound ($Co_xCu_y$). According to the suppression mechanism,

$As_2O_3$ and Cu will catalyse a kinetically suppressed cobalt deposition rate (Yang *et al.* 2006).

Many articles on cobalt removal from zinc sulphate electrolytes have focused on identifying different alloys that may form during cobalt cementation. It has been suggested that these cobalt alloys act as cathodic substrates for cobalt deposition (Yang *et al.* 2006, Zeng *et al.* 2006). Improvements in solution purification in sulphuric acid-based leaching solutions are evaluated in more detail in Paper 1.

Smaller plants using batch operation prefer the removal of copper and cadmium with zinc dust and subsequent purification of cobalt and nickel by α-nitroso β-naphthol (Singh, 1996). This process adds organic matter into the system and leads to high power consumption in the cell house. The advantage of this process is operation at low temperatures, because the solution does not require heating and little zinc is lost with the deposited material.

Most electrolytic zinc plants have to deal with dissolved magnesium in their recycled sulphate solution, due to zinc sulphide concentrates containing small amounts of magnesium, typically 0.2 wt.%. Residual fluoride can cause pitting of the aluminium cathodes in the electrowinning stage and the magnesium precipitation methods applied are generally expensive and environmentally unfriendly. It is possible to precipitate magnesium fluoride selectively from purified zinc sulphate solutions and convert the precipitated magnesium fluoride to magnesium hydroxide by contacting it with sodium hydroxide solution. The resulting sodium fluoride solution is treated in a membrane cell in order to regenerate zinc fluoride and sodium hydroxide solution (Booster *et al.* 2001).

### *2.4.1 Costs in solution purification*

All impurities have to be removed in the solution purification step if cost effective production in electrolysis is desired. Cost-wise, the best reagent for purification is zinc. Other metals could also be used, but they should be removed in the next step. Both removal of impurities and separation of valuable co-products (e.g. copper and cadmium) needs to be kept in mind when designing process improvements.

The hydrometallurgical process for separation and recovery of cobalt from a zinc plant residue consists of several unit operations: washing; roasting and leaching; selective precipitation; elimination of zinc, cadmium and copper from

cobalt; cobalt and nickel separation by solvent extraction; precipitation and calcination to cobalt oxide (Wang & Zhou, 2002).

The effect of organic reagents like tartrate, used to reduce foam formation and increase current efficiency in the cell house, has been studied in several papers, and they can have an adverse effect on the cementation rates (Bøckman & Østvold, 2000).

## 2.5 Electrolysis

The final step involves passing an electric current through insoluble electrodes to cause the decomposition (electrolytic dissociation) of an aqueous zinc sulphate electrolyte and the deposition of metallic zinc at the cathode with simultaneous regeneration of sulphuric acid. These two half-cell reactions are:

*Cathode*:
$ZnSO_4$ (solution) + $2e^-$ → Zn (metal) + $SO_4^{2-}$ (solution) (5)

*Anode*:
$H_2O$ (liquid) → $2H^+$ (solution) + ½ $O_2$ (gas) + $2e^-$ (6)

*Overall reaction*:
$2ZnSO_4$ (solution) + $2H_2O$ (liquid)
→ 2Zn (metal) + $2H_2SO_4$ (solution) + $O_2$ (gas) (7)

Aluminium cathodes have an oxide layer which provides a substrate from which plated zinc can be easily stripped, while at the same time preventing corrosion of aluminium in the corrosive acidic electrolyte. Lead anodes typically contain between 0.5–1 weight percent of silver. This kind of alloy possesses good corrosion resistance in the acidic electrolyte (Bond, 1999). Additives such as glue are added during electrolysis to limit the impact of impurities, facilitate the stripping of the zinc deposit and to prevent acid mist emission from the cell caused by gas evolution.

The control objectives for this process are to recover high-purity metallic zinc from the electrolyte, and to reduce the electrical power consumed during recovery. To achieve these aims, it is imperative to maintain the optimal electrolysis conditions. Expert control systems have been developed for effective process control of the electrolytic plant and e.g. a back-propagation network has been used; this is particularly useful in approximating the nonlinear relationships of complex processes (Wu *et al.* 2001).

## 2.6 Casting

At the conclusion of the electrolysis stage, the electrodeposited zinc is stripped off the aluminium cathodes by hydraulically operated stripping machines. The stripped zinc is melted and cast to commercial shapes. (Fugleberg, 1999)

## 2.7 Development in the process control

To obtain high-purity metallic zinc and reduce costs, the composition of the raw and purified zinc sulphate solutions must meet given standards, and the zinc in zinc concentrate must be dissolved as well as possible. Even small faults in the leaching equipment may lead to changes in flow rates or temperatures, which can be quite hazardous, so it is important to ensure that the process runs safely. This requires methods for effective control and fault diagnosis for the leaching process.

Since the 1980s, expert systems have been widely studied and applied to process control (Wu *et al.* 1999). An expert control and fault diagnosis scheme has been developed to improve control performance and ensure safe operation of the process. One possibility is to use an expert controller to determine the optimal pH of the leaching process and a fault diagnosis module to perform on-line and off-line fault diagnosis.

The models used are constructed from empirical knowledge, statistical data and chemical reactions (Wu *et al.* 2002). The control performance of iron precipitation in a flotation plant is evaluated with the development of a monitoring tool and applications (Jämsä-Jounela *et al.* 2003) In addition, failure analysis has been carried out to evaluate the reasons for rapid failures of the process equipment (Li *et al.* 2006).

## 2.8 Zinc production at Boliden Kokkola (known as Outokumpu Zinc until 2002)

The electrolytic process at Kokkola operates mostly according to the previous presentation, but with some exceptions:

In the conversion process, the leaching of zinc ferrite (the neutral leach residue) and the precipitation of jarosite and other impurities are performed simultaneously with a very high recovery (Fig. 5).

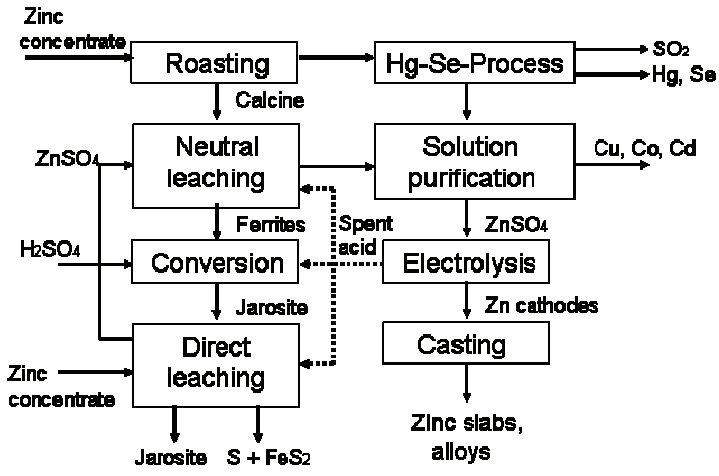


**Fig. 5. A block diagram of the zinc production process at Kokkola (Takala 1999). Concentrates are fed to the roasting and direct leaching processes. Concentrates more suitable for roasting are fed to the roaster, while the rest of the concentrates can be fed to direct leaching (Nyberg, 2004).**

Part of the leaching is done without roasting, which makes it possible to increase zinc production without any roaster expansion or increase in sulphuric acid production. In this direct leaching process, extraction of zinc well above 98% has been achieved with a number of available concentrates (Fugleberg, 1998).

In this direct leaching process, concentrate together with slurry from the conversion process, acid from the electrolysis and oxygen are fed to the reactors. Oxygen is an essential element in the leaching process, where it acts as a primary or secondary oxidant in the dissolution of sulphuric concentrates. The solubility of oxygen in dilute sulphuric acid environments depends on temperature, pressure and the salts present. The amount of the oxygen feed is defined experimentally in the direct leaching experiments on different sulphuric zinc concentrates (Kaskiala, 2002).

During the process the rest of the dissolved iron in the conversion solution and the iron dissolved from the concentrate are precipitated as jarosite. The zinc-containing sulphuric solution is separated from the slurry by flotation (Jämsä-Jounela *et al.* 2003).

Solutions from both leaching methods are combined and transferred to solution purification. In purification, the target is to remove impurities which will have a

harmful effect on electrolysis, either by contaminating the depositing zinc or by reducing the current efficiency. Valuable metals, like copper and cadmium, should also be removed with high selectivity into separate products. These co-products should also be in a form which makes refining into end products easy and economical.

At Kokkola, impurities are deposited with zinc dust in a continuous three-step purification process. The first step is copper cementation, where part of the copper is cemented and part of it is left to boost up cementation in the next purification process. The high-grade copper precipitate that is produced is sold to copper smelters. Cobalt, nickel, germanium and antimony are deposited with arsenic trioxide ($As_2O_3$) at a temperature of 70-75 °C. In the third and last step, cadmium is deposited using a fluidized bed system (Fugleberg, 1999). Between the second and third step, deposition particles are rigorously removed from the solution, because of the injurious effect of arsenic compounds on cobalt removal.

The amount of feed solution, arsenic trioxide solution, zinc powder feed and the process temperature, potential level and filtering pump pressures are measured on-line (measurements are further evaluated in Papers 1 and 2). The purification process is characterized by the low consumption of reagents (arsenic trioxide and zinc dust) and energy. The commonly used “hot arsenic zinc dust” purification method uses a higher temperature, 90-95 °C, to remove impurities, where high grade copper cement with low cadmium content can be produced.

The purified zinc solution continues to the electrolyte cells, where zinc is electrodeposited onto aluminium cathode sheets. During the reaction, the equivalent amount of oxygen gas and acid is produced. Acid is returned to the leaching process while oxygen bubbles disperse acid mist into the air and maintain operating conditions on the surface of the cell. About half of the electric energy consumed in electrolysis is converted to heat. Water evaporates from the heated zinc solution and is removed by circulating the solution through cooling towers. This water represents more than half of the water removed from the process. The water balance is recovered by thorough washing of residues.

Stripped zinc cathodes are melted in induction furnaces and the metal is cast into different shapes before being delivered to customers. Part of the produced zinc dust is used in the purification process to provide favourable conditions. This zinc dust is produced by atomizing molten zinc with air.

# 3 Evaluation of process data

In the measurement process, first measurements are taken; data is collected and then turned into information. This process also produces uncertainty, but if we look at several measurements, they also contain mutual information (Pyle, 1993)

Knowledge of the process dynamics and frequency of disturbances should shape the sampling strategy. In general, a sampling frequency 6-10 times that of the disturbance frequency will clearly differentiate disturbances from each other (Sanders, 1995). In industrial processes, laboratory analysis frequency, however, is most often based upon the importance to process control and costs rather than upon disturbance frequencies. As a result, a lot of sample analysis, which has cyclical trends or drifts, shows up as simple data noise. Information is lost and it is harder to isolate reliable causes.

Part of the available process data comes from on-line analysers, which produce data practically in real time and give information about changes in reactors. The disadvantage of these devices is their need for maintenance. Detectors wear out, contaminate and clog up every once in a while, depending on the type and application of the equipment. Measurement information gathered during this kind of situation includes attenuation and distortion in the measured signal or periodic zero values.

## 3.1 Measurements

A sensor – as handled in this paper - is a device consisting of one or more transducers and a transmitter which converts signals into a form recognizable by the control or monitoring system. Increasingly, the availability of local computing power has been exploited to carry out internal diagnostics within “intelligent” sensors.

In the widest sense, “sensor fusion is the synergistic use of a set of potentially inconsistent measurements from different sources” to achieve a specific task. A considerable amount of academic literature has been published in this area. For example, one study calculated that over 3000 papers were published on the topic of sensor validation as early as 1998 (Misra *et al.* 1998) and since then publishing activity has stayed at a high level.

Sensors can be roughly divided into critical and advisory. Critical sensors are used e.g. for controlling boiling reactors in power plants or on aircrafts. These critical measurements are usually monitored by several direct and indirect

measurements and complemented with process models and knowledge-based systems. In these cases, sensor redundancy is often augmented with reference measurements that are obtained from physical characteristics and/or a model of the plant dynamics in combination with other available sensor data. Both sensors and analytical redundancies are referred to hereafter as redundant signals.

In contrast, advisory on-line measurement provides information that is used to support control and to guarantee an undisturbed process. These measurements are mainly based on laboratory analyses, complemented by on-line sensors.

Laboratory analyses are commonly used in the process industry, but the purpose of the use and criticality of the analyses vary. Normally, analyses are used either to monitor the process, or to control or validate on-line measurements. If based solely on laboratory analysis, process control becomes inefficient due to the infrequency of analyses. On the other hand, laboratory analysis improves control when it is used to validate and correct on-line measurements.

In a mill environment with several on-line measurement devices, one on-line measurement device transmits measurements every few seconds or minutes, whereas samples taken from the same place are analysed in the laboratory usually only once or twice a day. Thus on-line measurements can be averaged, whereas off-line measurements are not duplicated and need to be reliable. For calibration and quality assurance, special samples may be collected, but the aim is that continuous monitoring of both on-line measurements and laboratory results of normal samples alone should be enough for effective process control.

## 3.2 Uncertainty of measurements

It is typical that the desired quantity cannot be measured directly (temperature can be measured several ways, i.e. from heat expansion, potential difference or from electrical resistance). Therefore, the quantity must be measured indirectly based on the dependency between the desired quantity and some measurable quantity. The dependency may be chemical, physical or discovered experimentally. Quantities other than those desired are usually regarded as disturbing factors, whose effect should be minimized. Indirect measurements are compensated to minimize disturbances. In practice, problems will arise after laboratory-scale tests where all of the disturbing factors may not be detected, or the calibration material does not include all the disturbing factors (Pyle, 1993).

In the case of an *optimal estimate*, the desirable property of estimate $\hat{x}$ of $x$ would be that:

$$E(\hat{x}) = x \quad (8)$$

According to this, the average value of the optimal estimate is the true value. Since all estimates are generally erroneous when compared to the true value due to uncertainties in the estimation process, it is natural to try to minimize this error (Liebelt, 1967).

Uncertainty of measurement means doubt about the validity of the measurement and is defined as a measured parameter. Uncertainty is normally associated with the result of a measurement. Another definition is the probability of a reading lying in a given range on either side of the mean value. Uncertainty can also be understood as a distribution (Weiss & Indurkhya, 1998). The Gaussian distribution is normally used to represent the distribution of measurements and the uncertainty of measurements.

Confidence-based uncertainty evaluation of quasi-redundant measurements was used for sensor self-validation and fusion by Frolik *et al.* (2001). In this application, the confidence level was used to measure agreement between the sensors. The methodology was based on:

1. Sensor self-validation (based on historical data), and the resulting quantitative and qualitative measures,
2. Sensor fusion incorporating these measures, and
3. Data reconstruction using several quasi-redundant sensors.

Uncertainty tries to quantify errors involved in measurements. The measurement errors can be roughly divided into systematic errors and random errors. Systematic errors (bias error) can be corrected, whereas a random error can be corrected by averaging several values. The magnitude of a random error in a measurement is typically represented as the confidence limit, which depends on the standard deviation ($\sigma$) of the measurement error. Usually, 95 % confidence limits are used in the case of the normal distribution ($2\sigma$) (Pyle, 1993).

In the case of 3-$\sigma$ control limits, 99.73 % of all values will be inside the limits, or in other words: the rate of false alarms is 0.27 %. If the control limits used are $2\sigma$, 95.46 % of all results and in the case of $1\sigma$, 68.26 % of all results will be inside the limits. If dynamic (adaptive) limits are used, the limits will change according to the changes in the chosen window (Fig. 6).

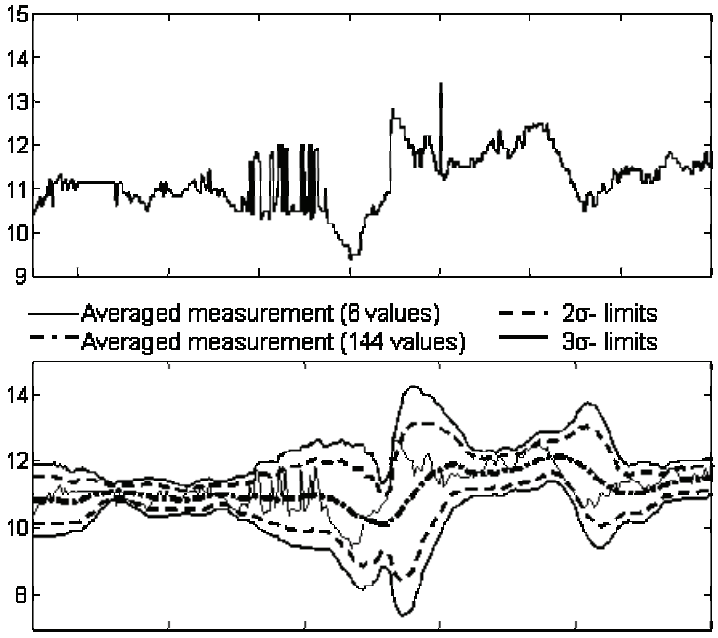


**Fig. 6. Example data (upper figure). Averaged measurements and adaptive 2 and 3 σ standard deviations, calculated in window of 144 measurements (lower figure).**

Methods for dealing with uncertainty include statistical process control, where the distribution of measurement errors and/or knowledge about the process are used to detect significant deviations. Fuzzy methods are also used to complete statistical analysis. Various process control methods can be effective in dealing with uncertain measurements, but they can be affected by measurement noise and errors. These outliers constitute a challenging problem in uncertain measurements (detecting them is much easier for a process engineer than for a computer). For example, outliers affect the standard deviation (σ) and the moving (±2σ) limits (dynamic confidence limits), allowing greater variations to be accepted in the next time window (Fig. 6). Estimation of uncertainty is based on variables linked to measurements such as process noise, sensor drift and sensor malfunction (Ng *et al.* 2000).

## 3.3 Statistical methods

The calculated correlation measures how variables are related (Wild and Seber, 2000). One of the most common measures of correlation is Pearson's correlation. Pearson's correlation itself was developed back at the beginning of the 20th century, but it is still a very useful method. The calculated coefficient reflects the degree of relationship between two variables (Pearson, 1907). The correlation coefficient is usually denoted by $R^2$ and can take values from -1.0 to 1.0, where -1.0 is a perfect negative correlation, 0.0 is no correlation and 1.0 is a perfect positive correlation.

Two variables can be perfectly related, but if the relationship is not linear, Pearson's correlation coefficient is not an appropriate statistical way for measuring their association and, for example, Spearman's correlation should be used (Fig. 7).

Like the $R^2$ value produced by Pearson's correlation, Spearman's correlation indicates agreement, but unlike Pearson's correlation, Spearman's rank correlation works on relative data, not directly on the data itself (Spearman, 1904) (Table 2).

In both correlation methods, a calculation is made of N pairs of measurements ($x_i$; $y_i$). In Spearman's correlation, the value of each $x_i$ is replaced by the value of its rank among all the other $x_i$'s in the sample. There is, of course, some loss of information in replacing the original values, but on the other hand, the nonparametric correlation is more robust than the linear correlation, in the same sense that the median is more robust than the mean.

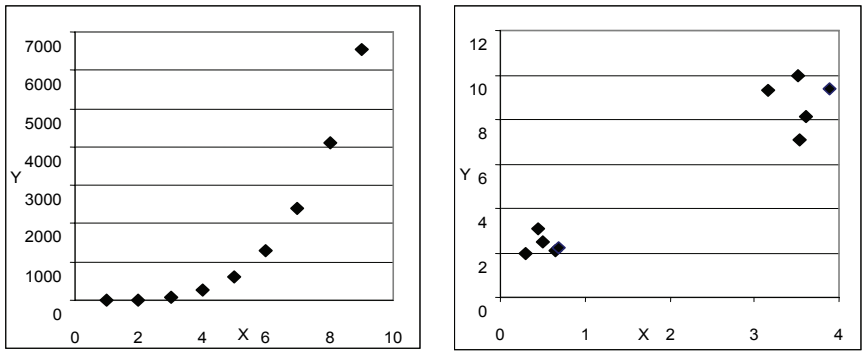


**Fig. 7. A: Correlation between X and Y:** **B: Correlation between X and Y:**

**Table 2. Correlation values for the example data (Fig. 7).**

| Calculation method | Value | Calculation method | Value |
|---|---|---|---|
| Pearson's correlation | 0.88 | Pearson's correlation | 0.96 |
| Spearman's correlation | 1.00 | Spearman's correlation | 0.76 |

## 3.4 Measurement validation

*Validation* can be described as a method for ensuring the accuracy of measurements. A sensor signal can be validated with additional information or by statistical analysis. The information may be an infrequent reference signal (laboratory analysis or calibration signal) or a signal produced by a mathematical process model. Sensor malfunction detection is an integral part of sensor signal validation. The information from a malfunctioning sensor may be used independently or accompanied with other information to validate a measurement (Henry & Clarke, 1993, Pyle, 1993).

*Calibration* – on the other hand - refers to the process of determining the relation between the output of a measuring device and the value of the measurement standard. In non-specialized use, calibration is often regarded as adjusting the output of a measurement instrument to agree with the value of the applied standard or reference measurement, within a specified accuracy (Ray & Phoha, 2000).

Individual signals in a redundant set may often exhibit deviations from each other after a length of time. These differences could be caused by several factors,

such as slow time-varying sensor parameters, plant parameters and transport delays. Consequently, some of the redundant signals can be detected and deleted by a fault detection and isolation (FDI) algorithm (Ray & Phoha, 2000).

On the other hand, failure to isolate a degraded signal could lead to an inaccurate estimate of the measured variable. For example, plant performance and stability may be adversely affected if an inaccurate estimate is used as an input to the decision-making or control system. Ray & Phoha (2003) presented a calibration and estimation filter for redundancy management of sensor data and/or analytical measurements. In their algorithm, signals were calibrated to compensate their relative errors and the weights of individual signals were adaptively updated as functions of the respective failure probabilities. This system smoothly calibrates each measurement as a function of its posterior failure probability, which is recursively generated based on present and past observations.

### *3.4.1 Sensor signal validation*

The use of process models in validation mainly follows the same idea as in the FDI. The self-validating (SEVA) approach incorporates sensor malfunction detection and measurement uncertainty estimation to produce a validated measurement (Henry & Clarke, 1993). In the SEVA approach, a corrective strategy is built to compensate the effects of the observed sensor failure (Duta & Henry, 2005).

In the case of one on-line sensor, data filtering (or data reconciliation) is based most widely on the Kalman filtering technique. This technique has been extended to several other applications to improve the accuracy of process variables or for data smoothing and parameter estimation. These techniques are developed for linear dynamic systems using weighted least squares as objective functions. In addition, methods for sensor malfunction detection based upon Kalman filters have been developed. Rollins *et al.* (2002) developed a method to handle biased measurements in a general fashion exploiting the gross error detection approach. Accuracy was improved through data reconciliation by detecting biased measurement. However, use of these applications is based on appropriate process models and the assumption that measurement noise is distributed normally.

Modern tracking-based methodologies, such as particle filter (PF) (Weiming *et al.* 2006), operate well beyond the Gaussian domain, but still need the process

model. In the case of the process data used in this application, the noise distribution is heavily emphasized (it has occasional zero values) and the measurement value tends to drift from time to time (as the measurement device deteriorates).

### *3.4.2 Multi-sensor data fusion*

Data fusion is one way to carry out dynamic data validation. Data fusion and integration are concepts for combining data from multiple sources to provide reliable and accurate information (Luo *et al.* 2002). The objective is to derive more information through combining than is present in any individual element of input data. Another aspect is to enhance the effectiveness of the sensor system by taking advantage of the co-operation of multiple sensors.

Multi-sensor data fusion is used in many military applications including automated targeting, battlefield surveillance and guidance, and control of autonomous vehicles (Ng & Ng, 2000). Non-military applications include monitoring of a complex process industry (Stork & Kowalski, 1999), robotics, medical diagnosis, biomedical systems, nuclear reactors (Ray & Desai, 1984) smart buildings and smart transportation systems (Luo *et al.* 2002).

The methods used in multi-sensor data fusion range from statistical to intelligent methods and multi-agent decision fusion for fault diagnostic has been used (Niu *et al.* 2007). When information from several sensors is combined, more "complex and intelligent" methods should be used (Luo *et al.* 2002).

Estimation of best measurement includes three possible ways of obtaining sufficient information to build a set of optimal signals. The first technique goes by the official title of "sensor redundancy." Critical process variables are monitored through independent channels and decisions are made using majority voting principles (Luo *et al.* 2002).

The second approach is based on the estimation of process variables from physical and chemical models using energy, momentum or mass balances and chemical equations. This method is known as "data reconciliation" or "analytical redundancy". In the third technique, empirical models may be constructed by estimating a function from a number of example input - output pairs with little or no knowledge of the form of the function (Ikonomopoulos & Van der Hagen, 1996). This problem has different names in different disciplines e.g. function approximation, system identification, data fusion/multi-sensor fusion, non-parametric regression, inductive learning and supervised learning. In the context

of signal validation, it is often known as "empirical redundancy" in accordance with the previous two terms. One of the goals of analytical and empirical redundancy is the detection of faulty measurements. Research in these fields of signal validation and fault detection has been extensive and summaries can be found for example from Rollins *et al.* (2002).

Process data validation includes an expert system with rules derived from operator experience. The rules include normal operating ranges and minimum/maximum limits for each variable. With continuous validation the errors are checked and alarms presented to the operator (May *et al.* 1992). Data reconciliation utilizing process model constraints (Narasimhan *et al.* 2000) is a method used to reduce random errors to improve the accuracy of the measurement through validation.

### *3.4.3 Statistical process control*

Several statistical methods are used to improve process performance and the quality of the outcome. Statistical process control (SPC) comprises a collection of statistical tools for data and process analysis as a basis for making inferences about process behaviour and opportunities for improving performance. Basic tools for improving quality are process flow charting (tells what is done), check sheets or tally charts (how often it is done), histograms (pictures or numeric data), graphs, Pareto analysis (prioritization), cause and effect analyses (what causes problems), scatter diagrams (relationships between variables) and control charts (monitoring variation and stability over time) (Oakland & Followell, 1990).

The goal of statistical process control is to eliminate variability in the process and to find abnormalities in process data. Using these tools requires no prior knowledge of statistics (Oakland & Followell, 1990). These simple chart techniques have proved powerful in monitoring process performance and in detecting abnormal events and their causes (Robinson, 2002).

Statistical process control uses continuous process monitoring to detect significant changes and disturbances in the process. However, these techniques do not provide explicit methods for adjusting the process. Process operators or quality control practitioners should have knowledge of how to use feedback or feed forward control and reliable enough measurements on which to base their control actions. In quality control, adjustment costs cannot be ignored. If an adjustment is expensive, or frequent adjustments are not feasible, it is reasonable to make adjustments only after breakdowns or significant deviations.

There are some weaknesses in the approach, particularly regarding normality and independence in the data. Statistical process control assumes that (Oakland & Followell, 1990):

1. The mean of the process measurements is constant;
2. The deviation of the measurements is constant.
3. Measurements are independent.

In the process industry, these prerequisites may be problematic, because the mean and deviation of process measurements varies as a function of time or as a consequence of breakdowns. In addition, detecting changes in the mean becomes difficult if the measurements are auto-correlated. Correlation between measurements is detected as a trend in the control charts, and that complicates interpretation when controlling the process. In continuous processes, almost all variables have some temporal correlation, even if the process is under statistical control (Oakland & Followell, 1990).

Statistical process control represents an area of data validation in connection with process control applications. Statistical process control is used in sophisticated error and outlier detection as well as in data fusion using various averaging methods (Luo *et al.* 2002). Instead of statistical process control, this work deals with problems of dynamic signal pre-filtering and confidence-based reasoning of on-line measurements based on reliable reference analysis. The result introduces a validation and estimation tool exploiting confidence levels and pre-filtered measurements for combining both laboratory and on-line signals.

Dynamic validation of on-line consistency and laboratory measurements was used by Latva-Käyrä (2003). He introduced a validation tool exploiting the exponentially weighted moving average (EWMA) of both laboratory and on-line signals and statistical reliability checks.

## 3.5 Sensor malfunction detection

A major problem in sensor malfunction detection is to distinguish between process changes and sensor failures. Especially in the case of a feedback control, sensor failures are often compensated by appropriate control action, which makes it difficult to detect the malfunctioning sensor. In sensor malfunction detection, redundancy, knowledge or measurement aberration-based methods can be used (Henry & Clarke, 1993).

In the process industry, an on-line measurement system is calibrated by using standard samples (e.g. weight scaling) or solutions (e.g. pH measurements), or comparing the measurements with laboratory analysis. The process is controlled in such a way to make reference measurements as accurate as possible in the current conditions. With the help of correction factors or functions, the sensor outputs are then processed to produce a signal similar to the original one. Self-testing and self-validating sensors have an internal signal reference, from where a validation signal can be fed into the sensor. From time to time sensor output is used to produce an error signal. Self-calibration is self-testing with a possibility of making changes in the sensor's transfer curve. However, self-calibration does not eliminate the need for traditional calibration. Calibration varies from simple calibration based on one laboratory sample to multisampling and multi-point calibration. The benefits of single-point calibration are fast and effective action connected with the demands of a narrow and stable operating range. This restriction does not occur with multi-point calibration, but the method is limited by the high workload it entails.

In redundancy-based approaches, duplicate measurements or a process model are used to generate a residual vector by comparing the measurements from multiple sensors or the output of the process model and actual measurements. The residuals can be examined using many methods in order to make a decision about sensor malfunctioning. Such methods include multi-sensor data fusion, voting systems, expert systems, artificial intelligence, fuzzy logic and neural network approaches (Amadi-Echendu, 1996). Model-based fault detection and identification (FDI) methods are thoroughly discussed in survey papers by Willsky (1976), Isermann (1984) and Frank (1990). Voting systems require three or more measurements of the same variable (Willsky, 1976). The deviating opinion (measurement) is ignored as the decision is made based on the majority of similar measurements. The voting system may include advanced characteristics as the differentiation between process upsets and sensor failures may be included in the reasoning (Stork & Cowalski, 1999).

Knowledge-based FDI systems exploit qualitative as well as quantitative models of the system (Frank, 1990). Through the qualitative models, additional information can be included into the FDI system. The additional information may include operational conditions, fault modes, signal behaviour characteristics due to a certain fault and historical fault statistics. The qualitative models are built and manipulated through heuristic knowledge. The knowledge-based FDI systems are discussed in more detail by Isermann (1997).

In degradation monitoring, the residual between the calibrated and original measurements represents the relative degradation of individual measurements. While large abrupt changes are easily detected and isolated by a standard diagnostics procedure, small errors (e.g., a slow drift) can be identified from the posterior probability of failure that is recursively computed from the history of residuals (Ray & Phoha, 2003).

In the measurement aberration approach, a single sensor signal is observed to detect sensor failure. It is based on the assumption that a true signal has certain properties, which remain constant. A deviation in a property indicates a possible sensor malfunction (Henry & Clarke, 1993). The properties can be statistical or based on the signal's time or frequency behaviour.

## 3.6 Self-validating sensors

In the SEVA (self-validating sensors) approach, the factors mentioned above are combined into a value that describes the uncertainty of measurement (Henry & Clarke, 1993). It is also proposed that the estimation of uncertainty in the SEVA approach is augmented with a sensor malfunction detection system, where sensor failures are classified and their impacts on the signal and uncertainty are estimated (Fry, 2002). However, variables like process noise, sensor drift or the impact of sensor malfunction are not necessarily easily defined. *The SEVA method is perhaps the closest example from the evaluated methods compared to the calculation algorithm presented in this work.*

A self-validating sensor performs additional processing to measure the validity of each measurement. The validated measurement value (VMV) is an estimate of the true value, and takes into account all diagnostic information (Fig. 8). If a fault occurs, then the VMV is corrected to the best ability of the sensor. In the most severe cases where the raw data is judged to have no correlation with the estimated variable, the current VMV is extrapolated from past measurement behaviour (Duta & Henry, 2005).

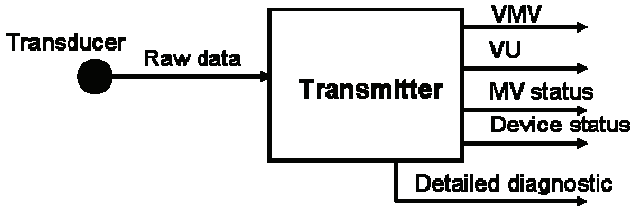


**Fig. 8. Construction of a self-validating sensor (Duta & Henry, 2005)**

The validated uncertainty (VU) is the uncertainty associated with the VMV. The VU gives a confidence interval for the true measured value. The VU takes into account several sources of error, including noise, measurement technology and any fault-correction strategy currently being used. The measurement value status (MV status) is a discrete-valued and indicates how reliable the calculated VMV is. The basic categories for measurement value status are shown in Table 3 (Duta & Henry, 2005). The device status assists users in determining whether the measurement is acceptable in the used application.

**Table 3. Different possibilities for measurement value status (Duta & Henry, 2005).**

| SEVA category | Definition |
|---|---|
| SECURE DIVERSE | The VMV is derived from multiple values of the same measurement at least two of which are CLEAR or better and which are not susceptible to common mode faults. |
| SECURE COMMON | The VMV is derived from multiple values of the same measurement at least two of which are CLEAR or better, but which are susceptible to common mode faults. |
| CLEAR | The VMV is calculated normally. |
| BLURRED | The VMV is based on live data, but is being corrected for a fault. |
| DAZZLED | A transient state: The VMV is based on historical data while the fault is assessed. |
| BLIND | No credible data is available. The VMV is being projected from past behaviour. |
| REPLACED | The VMV comes from an external agent (operator or higher level modelling program). |
| OFFLINE | The instrument if off-line. The VMV and VU are typically zero. |
| UNVALIDATED | Validation not in operation. |

The data used in this work is rarely distributed normally or even close to it. Unfiltered data includes high peaks (erroneous measurements), which distort distribution and also increase the calculated standard deviation.

In Papers 3-5, uncertainty is not estimated through estimations of certain variables but instead is associated with process dynamics. This can be done thanks to the reference signal, which is assumed to be highly reliable. The reference signal gives not an estimate but a real measured value, which can be used to evaluate the accuracy of the sensor. The dynamics of the process can be obtained from the data as statistical values or from expert knowledge. In this work the term confidence is used instead of uncertainty. The calculation of confidence levels are discussed further in Paper 4.

# 4 Summary of papers

Papers 1 and 2 evaluate results from the first research project, where the target was to collect knowledge from solution purification and combine process data with chemical reaction models. The second project (Papers 3-5) concentrated on improving controllability in the direct leaching process. In order to achieve this target, a calculation algorithm, called "calculation of optimal estimate", was created to combine process data.

## 4.1 Technical details

During the research project PRODYNA, the second step of solution purification, cobalt removal process, was changed from a batch process to a continuous purification process. This modernization was preceded by a detailed pilot-scale process, which was used alongside the batch process for several months to ensure the required purification power, stable conditions and reliable purification results.

The pilot-scale equipment (described in Paper 1) consisted of four series-connected 580-litre stirred tank reactors and one 250-litre thickener. The supply stream was 650 l/h, the return feed from the thickener was 220 l/h and the process temperature was 80º C. Solids were periodically discarded from the thickener to keep the recycling load approximately constant. The amount of this circulated deposit was one of the parameters studied, but according to the results, the composition of the deposits was more important than the total amount. The study was a continuation of the laboratory tests done at the plant and intended to be one step closer to process conditions.

Part of the measurements were collected at the minute level (amount of feed solution, used reagents and temperature), while solution samples from each tank and one combined deposition sample from all reactors were normally collected once a day and in intensive research every 4 h (deposit features varied so slowly, that this kind of analysis frequency was sufficient). The total test period in the pilot-scale process took over one year and in the case of solution filtration (Paper 2) over six months.

In the cobalt removal process (and similarly in the pilot-process) all the solution and deposit analyses were done in the laboratory. Elements like Al, Fe, Co, Ni, Cu, Zn, Cd, Si, Ca, As and Sb (concentration around 1–2 mg/l) were analysed from the solution samples by ICP-AES. An X-ray fluorescence analyser was used to analyse Ge, Co, Ni and C concentrations after deposition and drying.

The back titration value, which describes the capability of solutions to buffer an acid feed, was analysed in the laboratory by back titration. The deposited elements Al, Fe, Co, Ni, Cu, Zn, Ge, As, Cd, Sb, Si and Ca from the cobalt removal process were analysed from a dried and compressed briquette directly by the X-ray fluorescence analyser.

In the direct leaching process, overall zinc extraction is around 97%, although the temperature is kept below 100°C. Oxygen is fed into acidic slurry, which enables the leaching of the zinc from its sulphide compound. The sulphuric acid concentration is 10-40 g/l and elemental sulphur is produced simultaneously in the same process.

In this case, the target was to develop an adaptive calculation method, which could be implemented without exact knowledge from the dynamics of the target process. In the calculation of this "optimal estimate", direct leaching process data from the $H_2SO_4$ and $Fe^{2+}$ on-line analyser were complemented with laboratory analyses (done twice a day). Calibration of the automatic analysers is done on average once in month and is based on laboratory analyses. From time to time inaccurate recalibration causes bias error and the measurement device can also deteriorate between calibration points. Exact knowledge of the analysis methods was not included in this work because the calculation algorithm does not take measurement technology into account.

## 4.2 Papers 1-2: Cobalt removal process

In the cobalt removal process, the purification reaction consists of three phases: solid zinc with deposited components, liquid containing zinc sulphate and gas (hydrogen) phase. A small-scale galvanic cell around the zinc particles creates circumstances where deposition can occur, even though overall deposition potentials in the reactors do not enable these reactions. As a consequence, it was necessary to test the interactions of several solution and deposit components.

The composition of the purified zinc-solution fluctuated during this research, causing variations in the solution and deposit components. There were also variations in the amount of the reagents added (arsenic feed, acid feed and zinc feed) and target conditions (potential in reactors and buffering capacity), in the attempt to achieve optimal conditions. Cross-correlations were calculated between measured variables and calculated deposition efficiencies. Before calculating correlation coefficients, the data was screened for outliers.

The introduction of the first article concentrates on the evaluation of the reaction kinetics by collecting published papers and knowledge from the factory. In the Kokkola case, the removal of impurities is done hydrometallurgically in three steps using zinc powder and $As_2O_3$. In reality, the reactions are more complex than presented in classical deposition reactions and several authors have continued the evaluation of the reaction kinetics. In this thesis, knowing the exact deposition mechanism was not essential, because the effect of reagents, catalysts and inhibitors was evaluated by data-based methods.

The purpose of this work was to develop a method of evaluating the success of the continuous purification process i.e. to calculate deposition efficiencies for the four different impurities and find out the influence of the solution and deposition components on the deposition efficiencies.

Cobalt deposition tests were done in the pilot-scale equipment and the collected data was evaluated using correlation analysis. In these analyses, the deposition rate was calculated for four different elements and process parameters affecting this variable were studied. Changes in the process and also in the pilot were slow, so the total test period was over one year.

The efficiency for each impurity and for all four reactors is calculated by the equation:

$$C_{eff} = \frac{(c_{x-1} - c_x) * F}{c_x * V} \tag{9}$$

where

- $C_{eff}$ is the deposition efficiency for reactor x,
- $c_x$ is the concentration of deposited impurity in the reactor (mg/l),
- F is the feed flow (l/min) and
- V is the reactor volume.

The results provided the impetus to develop quantities that better describe the real effect of the depositing components of feed solutions. This was done by calculating weighted moving averages (accumulation) for the depositing elements. The delay (or lead-time) in the deposition reactors is only a couple of hours, but features of the deposited material, which catalysed the deposition reaction, change over a much longer time period. The calculation concerned the last 100 h linearly, where the first value was given the weighting factor of 0.01 (100h backwards from the calculation point) and the latest value was given factor

1. In this way small-scale variation was removed and real effects with higher correlation values were achieved.

The second paper concerns the real process data from the continuous purification process and evaluates the reasons for filtration problems. The behaviour of the filtration pressure is evaluated in good and problematic process conditions together with factors that have an effect on the pressure during a longer time period. In the production-scale continuous solution purification process, effective filtration of the cobalt deposit before the subsequent purification process is also needed.

When the depositing material forms permanent and spherical granules, it enables the formation of a thick layer of deposit on the cloth screen. In optimal conditions, the filtration pressure is stable and does not grow even though the deposit layer gets thicker. However, in problematic situations, even a small amount of deposit may create a nearly impermeable layer. Poor permeability leads to the use of high pump pressure and risks of breakage.

During the research period, filtration pressure varied widely and thus cross-correlations were calculated for three different sets of data. Process data was also used in this case for the calculation of correlation values between the pump pressure and measured process parameters. In the first period, filtration problems were generated slowly and optimal conditions were not found. In the last period, the process conditions were close to optimal with only slight changes in the pressure.

The drifting from one operating range to another and changes in the blocking sensitivity of the filter can be seen from several process variables. For example, the acid feed has a strong negative correlation with the pressure in the largest data set, a weaker correlation in the first set and a zero correlation in the last set. With low acid feed values, even a small deviation leads to a strong change in pressure, and with a high acid feed, even strong alterations in the acid feed have no more than minor effects on pressure. In addition, the scatter plot analysis revealed two minor operating ranges. In these areas, a relatively high acid feed and high pressure values are present at the same time.

This behaviour is explained by changes in the deposited material. When the acid feed is small, the deposited granulates are flat and tend to form an impermeable layer under pressure. If the acid feed is high enough (and other process parameters such as the zinc and arsenic feed are in the right range), the granules are round and form a highly permeable layer.

### 4.3 Papers 3-5: Calculation of the "optimal estimate"

Information from process measurements should be processed into the form, which provides maximum help to operators with control procedures. Papers 3-5 present a confidence level-based calculation algorithm, called "optimal estimate", for combining real-time redundant signals, consisting of sensor data and reference measurements. The calculation does not exploit estimation theory, but estimates the reliability of measurements and on this basis calculates the "best guess" from the available data.

The validation of on-line measurement uses less frequently updated but more accurate information to validate frequently updated but less accurate on-line measurements. An estimate of the measured variable is obtained as a weighted average of the on-line measurements and laboratory analyses. The weighting coefficients are recursively updated in real time when new analysis and measurement results become available. The calculation of the "optimal estimate" can be used in several industrial applications for more precise process control.

With proper data fusion, the advantages of original signals are adopted in a reliable continuous-time signal. This sounds easy, but when building an estimation algorithm that works with the plug and play technique, fusing information turns out to be a complex task. The type of data varies depending on the source of the information. For example, the data may be sparse, noisy or contain varying process delays, and reference measurement may have different analysing delays, all of which have an essential role in data fusion.

When sorting out which measurements are real and which erroneous, there is a need to settle the range for each process parameter. The feature that is probably easiest for us is the minimum and maximum values of the variable. These absolute limits define values, which are beyond the range of the variable and can be directly classified incorrect. These limits are obtained from data or prior knowledge. Fuzzy regions are used to narrow this relatively wide range to respond better to different process conditions.

The second important feature of the measured variable is the mean. In a long time period, the mean value of the variable should remain constant - assuming there are no changes in the set points of the process. In a shorter time period, the mean value fluctuates due to normal process variations. Standard deviation (or variance) tells us how widely the measurements are spread around the mean value and this should also remain constant during a long time period. As a consequence, changes in the *standard deviation* (or variance) *and mean are commonly used as*

*indicators for sensor malfunction.* A varying standard deviation and mean are caused mostly by process changes or sometimes by a malfunctioning on-line measurement device. To evaluate the validity of a measurement it is essential to distinguish between process changes and a malfunctioning sensor. In the dynamic validation of on-line measurement faults are ruled out and a corrected signal is used to adjust the process.

In this application, the validity of the measurement is not evaluated directly through changes in the standard deviation or mean value. Instead, the minimum and maximum values are used together with data-based reasoning, like maximum changes in the time window and maximum changes between consecutive measurements.

In the cases of varying process parameters it is natural to consider the use of fuzzy control limits. For example, if the data range varies greatly (process conditions are changed advisedly), real hard limits are not very useful. In the application developed here, a fuzzy region lies between the fuzzy and absolute limits where it is not certain if the measurement is valid or invalid. In this region, the weight of the measurement (given as a membership function) decreases from reliable (weight 1) to non-reliable (weight 0) (Paper 3).

In the case where fuzzy limits are defined as constant, the detection of an invalid measurement depends on the process conditions. If the measured value is close to the maximum or minimum limit, the deviating measurements will more likely lie in the fuzzy region than in a case where the operating point is far from the absolute values. In consequence, fuzzy limits, which are adaptive and change with the process conditions, were used. This was implemented using the standard deviation and in the latest version a modified (standard) deviation. If the standard deviation was used for the calculation of adaptive limits, greatly varying measurements expanded the dynamic limits and possibly invalid measurements were classified as valid (instead of being erroneous) (Paper 5). Limiting the significance of one deviating measurement reduced changes in the fuzzy boundaries and enabled direct use of measurement validation without any prior reasoning.

In the calculation of an estimate, the following components are used:

- pre-processed on-line signal, where outliers are replaced by corrected values ($X_{classifier}$)
- reference signal (laboratory analysis) ($X_{ref}$) and
- calculated confidence level of on-line signal ($C_{measurement}$) and

– calculated confidence level of reference measurement ($C_{ref}$)

In the algorithm, coefficient ($1 - C_{measurement}$) is used to decrease the weight of the confidence level of the laboratory analysis. The idea is that the corrected on-line signal is always to be trusted when its confidence level is relatively high. The estimation algorithm is:

$$X_{estimate} = \frac{C_{measurement} X_{classifier} + (1 - C_{measurement}) C_{ref} X_{ref}}{C_{measurement} + (1 - C_{measurement}) C_{ref}} \tag{10}$$

The important features of the calculation of the estimate are:

– A model of the physical process or expert knowledge is not needed for the successful calculation of the estimate. Only the prominent data period of measurement device data and reference measurements are needed for the basis of process parameters (range and maximum step) estimation.
– The pre-processing manipulates measurements that are beyond the fuzzy limits of the dynamic range of the variable and by correcting the static error between the measurement device data and the reference measurement.
– The confidence level of the measurement is determined by the deviation of the measurement from the laboratory analysis and by changes between individual measurements. In contrast, the confidence level of laboratory analysis is only time-dependent. The weight coefficients of the on-line signal and laboratory measurements are adaptively updated.
– The calculation of the estimate tends to trust the measurement whenever its confidence level is relatively high and to use laboratory analysis only for bias correction.

The information produced in the calculation of the optimal estimate is also used for calculating the on-line deterioration (need for maintenance) indicator (Paper 4). This indicator is based on changes in the standard deviation of the measurement. As long as a measuring device works properly, the standard deviation stays almost constant. Standard deviation varies with process conditions, but on a smaller scale. In the case of deterioration, standard deviation either grows (the measuring device oscillates) or converges depending on the device. Results from the indicator fall into two categories: the need for calibration and warning of breakdown — depending on how the application is adjusted. Warnings may contain information about problems in the measuring device (on-line analysis is not reliable and estimate is based mainly on the laboratory

analysis). Beginning deterioration is compensated in pre-processing and in the calculation of the estimate, but confidence values and confidence of the estimate decreases gradually, until the measurement device is repaired.

The large complex of data pre-processing, the calculation of the "optimal estimate" and the need for a maintenance indictor is divided into three papers. *Paper 3 presents the calculation of the confidence-based "optimal estimate" and signal pre-processing. The fourth paper improves the usability of the calculation by presenting the on-line deterioration (need for maintenance) indicator.* Together these two calculation algorithms build up a useful system for a large range of applications. *In the last paper, signal validation and outlier detection is modified for varying process conditions using adaptive fuzzy limits in signal pre-processing.*

# 5 Conclusions and discussion

The aim of the thesis was to increase the value of existing measurement information by determining the dynamics between process parameters and by combining measurement data to produce accurate estimates from the process state. Together these will increase the usability of existing measurements without investment in new measurement devices.

Controller performance is highly dependent on the reliability of information which is received from measuring devices and from reference measurements. Measured process data is inherently inaccurate and these measurement errors can be caused by random noise, deteriorating, malfunctioning or wrongly calibrated instruments.

The literature written in this area describes a large number of techniques for sensor validation, starting from principle component analysis, Kalman filters, particle filters, knowledge base systems and neural networks - a whole range of methods, which require application-specific learning, modelling and tuning. What separates this approach is that:

- It produces a confidence value for each measurement and for each reference value.
- The calculation of confidence level uses direct data-based reasoning (limits are based on the standard deviation of the measurement), expert knowledge or a combination of these two.
- In addition, the data fusion technique described here is entirely model-free and, hence, suitable for implementation after light configuration within an automation system, requiring virtually no modelling or tuning.

The data validation method that has been developed combines information from laboratory analyses and measurement device data to calculate the “optimal estimate” of the actual process variable. This reconstructed data is then passed to operators or used by the controller (the estimate can be applied as a part of the advisory or direct control strategy depending on the target process).

In Papers 1 and 2 correlation values were calculated for different data sets from the pilot-scale process to industrial-scale production. Variations in the results of both cases illustrate how easily apparently correlating variables can be found by choosing a suitable time period. When providing data-based analysis to the production process, several factors need to be taken into account before continuing to the evaluation of the results:

1. Only prolonged research periods and systematic changes in the process create process parameters that influence the larger operating range.
2. Simultaneous changes in several process parameters should be avoided (if possible).
3. Data analysis should be conducted on several data sets and the results compared to avoid false interpretations.

The correlation analysis used here applies conversely in process control. For instance, by observing the correlation between certain process parameters and pressure, operators may foresee the sliding of the process towards problematic areas and prevent it by making corrective changes before a filtration problem develops.

The results have been exploited in the process control of solution purification. In the case of the cobalt removal process, it was necessary to get the continuous solution purification process working reliably and with a high enough deposition efficiency, especially because there was no possibility of adding reagents and increasing deposition time as there was in the batch process. The evaluation of deposition mechanisms and the effect of the amount of different reagents on the calculated deposition efficiency were also current, even though the $As_2O_3$ - activated deposition reaction was known and had been in commercial-scale use for decades.

According to the results, the concentration of the depositing elements in the feed solution affects the deposition efficiency over a much longer time period than a process delay in the reactors would presuppose. Positively affecting components were a high copper content in the feed solution and a relatively low arsenic content, when compared to the target value.

When finding out solution filtration problems, the highest and most immediate benefit to process control was getting the filtration process working properly again - and secondly to obtain knowledge and new information about the level at which the controlled process parameters (potential level/zinc powder feed) should be to ensure that filtration problems would not occur again in the future.

The statistical methods used were found to be suitable for the evaluation of pre-processed data. When sorting out deposition mechanisms and filtration problems, more complex modelling methods could also have been used. The problem in this work was that none of the measured variables correlated with calculated deposition efficiency (the surface activity of deposits cannot be

measured). In this case, problems are easily compounded with the interpretation of results – whether they are realistic or not. Even statistical analysis resulted in situations where correlation values between variables differed widely between data sets. If e.g. fuzzy models or neural networks are used in this kind of situation, problems are easily caused when the model is fit to a data set that is not representative during a longer time period.

Intelligent modelling techniques could have been useful only in situations where the deposition efficiency was estimated by calculating weighted moving averages (accumulation of affecting elements). On the other hand, a combination of linear regression models might have been accurate enough.

Instead of exact deposition models, it is much more useful for process control to have case-specific limits and the estimation that when these limits are crossed, problems will be generated (this applies to both deposition efficiency and filtration problems).

Papers 3 to 5 described an adaptive calculation procedure for the estimation of the measured plant variable when a reference signal is available. The reference signal can be a reference (laboratory) measurement or other process information that is estimated to be more accurate than validated on-line measurement.

The limits used in data validation have proven to be critical, since too strict limits give laboratory analyses an unnecessarily big weight and lose fast and short-term changes in the process. On the other hand, limits that are too wide allow faulty measurement device readings to be accepted and used in further process control (measurement device malfunctions are not differentiated from process disruptions). If a faulty measurement device is detected (measurement device readings change more rapidly than process dynamics will allow or if the signal is not inside the area of operation), the estimation algorithm tends to follow laboratory analysis and only when possible takes advantage of the measurement device data.

Reliability estimation (calculation of confidence levels) done by a calculation algorithm, diminished the need for operators to make their own interpretations of the reliability of the measurements. Moreover, the calculated “optimal estimate” is not dependant on the operator. It is quite possible that different operators would make varying interpretations of the difference between measurement and reference analysis.

An on-line deterioration indicator improves the predictability of breakdowns/need for maintenance and speeds up corrections when used effectively. Numerical values from the usefulness of both estimation and

deterioration algorithms are difficult to obtain, because of the lack of reference measurement.

The algorithm developed complements the high variation of signal validation and estimation methods presented in the literature. However, the calculation algorithm of the "optimal estimate" has the potential to be exploited more widely in applications that are not important enough to have their own process models and sensor technology-based signal validation models but where measurement is useful for process monitoring.

The implementation of the development stage calculation algorithm was done in 2004 and since then it has been working properly in the direct leaching process. More practical testing would have been useful for evaluation of whether the estimate is robust enough to work properly in different process environments. The portability of the estimate was the starting point for its design, so according to the experience gained, as long as the training data is prominent (or is complemented by expert knowledge) problems should not exist. In the future research work, calculation algorithms will be exploited when possible.

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ISBN 978-951-42-8490-8 (Paperback)
ISBN 978-951-42-8491-5 (PDF)
ISSN 0355-3213 (Print)
ISSN 1796-2226 (Online)