Theresa Verena Grabmayer, BSc

Optimization of the use of substitute raw materials and substitute fuels in cement production

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Ao.Univ.-Prof. Dipl.-Ing. Dr.techn. Klaus Reichmann

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AFFIDAVIT

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Abstract

The aim of this work is the development of an assessment and control tool for cement production in the form of a mass balance. As a result, the influence of substitute raw materials and substitute fuels on the properties of cement products, the process stability and efficiency as well as on the CO_2 emissions and heavy metal content in the product can be better controlled and used in a targeted manner for the best possible cement quality. The analysis behind it is fundamental for this. On the basis of a round robin study, the X-ray fluorescence analysis (XRF) is regarded as a fast and proven analysis method in cement production. In order to be able to assess and efficiently manage the procedural aspects, such as the cycle formation of alkalis, sulphur and chloride, the calibration of the XRF with respect to the alkalis sodium and potassium, sulphur and chloride had to be extended for the process samples, which represents the chemical focus of the work. In addition, grinding tests were carried out on the process samples in order to exclude any matrix effects due to the sample preparation (grinding time, chemicals used) during XRF. With the developed mass balance, the chemical, procedural, legal and economic challenges due to the increasing use of substitute raw materials and substitute fuels can be met in a targeted manner and the potential of future input materials can be identified and assessed.

Kurzfassung

Ziel dieser Arbeit liegt in der Entwicklung eines Beurteilungs- und Steuerungstools für die Zementherstellung in Form einer Massenbilanz. Dadurch kann der Einfluss von Ersatzrohstoffen und Ersatzbrennstoffen auf die Eigenschaften der Zementprodukte, die Prozessstabilität und -effizienz sowie auf den CO_2-Ausstoß und Schwermetallgehalt im Produkt besser kontrolliert und für eine bestmögliche Zementqualität gezielt genutzt werden. Von grundlegender Bedeutung dafür ist die Analytik dahinter. Auf Basis einer Ringversuchsstudie gilt die Röntgenfluoreszenzanalyse (XRF) als ein schnelles und bewährtes Analyseverfahren in der Zementherstellung. Um die prozessualen Aspekte, wie die Kreislaufbildung von Alkalien, Schwefel und Chlorid, beurteilen und effizient steuern zu können, musste die Kalibration der RFA von den Alkalien Natrium und Kalium, Schwefel und Chlorid für die Prozessproben erweitert werden, was den chemischen Schwerpunkt der Arbeit darstellt. Zudem wurden Mahlversuche von den Prozessproben durchgeführt um etwaige Matrixeffekte aufgrund der Probenvorbereitung (Mahldauer, verwendete Chemikalien) bei der RFA auszuschließen. Mit der entwickelten Massenbilanz können künftig die chemischen, prozessualen, rechtlichen und wirtschaftlichen Herausforderungen durch weiter steigenden Einsatz von Ersatzroh- und Ersatzbrennstoffe zielgerichtet bewältigt und das Potential zukünftiger Einsatzstoffe identifiziert und beurteilt werden.

Content

AFFIDAVIT I

ACKNOWLEDGEMENT II

ABSTRACT III

KURZFASSUNG III

LIST OF FIGURES VI

LIST OF TABLES VIII

LIST OF ABBREVIATIONS X

1 INTRODUCTION 1

2 STATE OF THE ART 5

- 2.1 CEMENT PRODUCTION PROCESS 5
- 2.2 DESCRIPTION OF THE INPUT MATERIALS 11
  - *2.2.1 RAW MATERIALS 11*
  - *2.2.2 SUBSTITUTE RAW MATERIALS 12*
  - *2.2.3 CORRECTION MATERIALS 13*
  - *2.2.4 CEMENT ADDITIVES 14*
  - *2.2.5 SOLIDIFICATION REGULATORS 14*
  - *2.2.6 FUELS 15*
  - *2.2.7 ALTERNATIVE FUELS 15*
- 2.3 PRINCIPLES OF SAMPLING AND SAMPLE PREPARATION 16
  - *2.3.1 PROCEDURE FOR SAMPLING 16*
  - *2.3.2 PROCEDURE FOR SAMPLE PREPARATION 18*
- 2.4 ANALYSIS METHODS 19
  - *2.4.1 CALORIMETER 19*
  - *2.4.2 CSA - CARBON-SULPHUR ANALYSER 20*
  - *2.4.3 ICP-OES - OPTICAL EMISSION SPECTROSCOPY WITH INDUCTIVELY COUPLED PLASMA 21*
  - *2.4.4 XRF - X-RAY FLUORESCENCE ANALYSIS 22*
- 2.5 PROCESS OPTIMIZATION 26
  - *2.5.1 RAW MEAL SPECIFICATIONS 28*
  - *2.5.2 INFLUENCE OF THE INPUT MATERIALS ON KILN OPERATION 28*
- 2.6 LEGAL ASPECTS 36
  - *2.6.1 WASTE MANAGEMENT ACT 37*
  - *2.6.2 WASTE INCINERATION ORDINANCE 38*
  - *2.6.3 TECHNICAL PRINCIPLES FOR THE USE OF WASTE AS REPLACEMENT RAW MATERIALS IN PLANTS FOR CEMENT PRODUCTION 39*

3 EXPERIMENTAL PART 41

- 3.1 MATERIALS 41
  - *3.1.1 RAW MATERIALS 41*
  - *3.1.2 SUBSTITUTE RAW MATERIALS 41*

3.1.3 Fuels 42
3.1.4 Alternative fuels 42
3.1.5 Correction materials 43
3.1.6 Solidification regulator 43
3.1.7 Additives 44
3.2 Quality assurance 44
3.2.1 Description of the analyses 44
3.2.2 Procedure of quality assurance for routine samples 46
3.2.3 Procedure of quality assurance for process samples 49
3.2.4 Procedure of quality assurance for additives and solidification regulators 49
3.2.5 Procedure of quality assurance for alkali, sulphur and chloride calibration samples 50
3.2.6 Procedure of quality assurance for grinding test samples 52
3.3 Analysis Methods 54
3.3.1 RFA 54
3.3.2 ICP-OES 55
3.3.3 CSA 56
3.3.4 Calorimeter 56
3.4 Evaluation methods 56
3.4.1 Excel 56
3.4.2 LIMS – Laboratory Information Management System 57
3.4.3 Assessment 57
4 EVALUATION 59
4.1 Development of the material balance 59
4.1.1 Theoretical calculation of the system using LSF, SR and AR 61
4.2 XRF as an alternative method to ICP-OES (round robin test) 65
4.3 Optimization potential through improved calibration for alkalis, chloride and sulphur and error analysis 73
5 CONCLUSION AND OUTLOOK 82
APPENDIX XIII
LITERATURE XXVIII

List of Figures

Figure 2.1: Flow chart of the cement production at the Wietersdorf plant using the dry process. . 6
Figure 2.2: Three-component diagram CaO-SiO_2-Al_2O_3+Fe_2O_3.[12] ... 8
Figure 2.3: Selected extraction points (in the middle and approximately 500 mm from the sides) for bulk goods, transported in trucks up to 15 t.[34] ... 17
Figure 2.4: IKA C 7000 calorimeter and the principle of double dry analysis. [37] ... 20
Figure 2.5: Analytical flow diagram of a carbon-sulphur-analyser CSA [41] ... 21
Figure 2.6: Schematic structure of an ICP-OES. [43] ... 22
Figure 2.7 Schematic structure of an XRF.[46] ... 23
Figure 2.8: Principle of X-ray fluorescence analysis [47] ... 23
Figure 2.9: Vapor pressure of the chlorides (left y-axis) and sulphates (right y-axis) of sodium and potassium as a function of temperature. [65] ... 30
Figure 2.10: Sketch of the mixing and inlet chamber with drawn oryfice of the kiln system in the Wietersdorf plant. ... 32
Figure 2.11: Temperature recording of a mantle screening of the rotary kiln in the Wietersdorf plant. ... 35
Figure 3.1: Limestone quarry in Wietersdorf ... 41
Figure 4.1: System boundaries (red dashed line) of the material balance for process optimization. ... 59
Figure 4.2: System boundaries (red dashed line) of the material balance for compliance with the heavy metal limit values. ... 60
Figure 4.3: Structure of the established mass balances. ... 64
Figure 4.4 shows which variants and methods are suitable for analysing the individual elements using XRF. If the recovery rate is between 70-130 % it is shown by mark '++'. [72] ... 70
Figure 4.5: Overview of all XRF results using the determined z-scores.[72] ... 72
Figure 4.6: Calibration line for sodium from the clinker samples (left with new mixed samples, right old calibration line). The chemical concentration of Na_2O in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis. ... 75
Figure 4.7: Calibration line for potassium from the raw stone samples (left with new mixed samples, right old calibration line). The chemical concentration of K_2O in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis. ... 76
Figure 4.8: Calibration line for potassium from the clinker samples (left with new mixed samples, right old calibration line). The chemical concentration of K_2O in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis. ... 77
Figure 4.9: Calibration line for potassium from the hot meal samples (left with new mixed samples, right old calibration line). The chemical concentration of K_2O in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis. ... 78
Figure 4.10: Calibration line for sulphur from the raw stone samples (left with new mixed samples of limestone, right with new mixed samples of marl). The chemical concentration of SO_3 in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis. ... 81

Figure 0.1 shows the calibration lines of raw stone for potassium, sodium and sulphur. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side. XXIII
Figure 0.2 shows the calibration lines of raw meal for potassium, sodium, sulphur and chloride. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side. XXIV
Figure 0.3 shows the calibration lines of hot meal for potassium, sodium, sulphur and chloride. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side. XXV
Figure 0.4 shows the calibration lines of clinker for potassium, sodium, sulphur and chloride. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side. XXVI
Figure 0.5 shows the calibration lines of bypass dust for potassium, sodium, sulphur and chloride. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side. XXVII

List of Tables

TABLE 2.1 LISTS THE PROCESSES THAT TAKE PLACE DURING CEMENT PRODUCTION IN THE DIFFERENT TEMPERATURE RANGES, AS WELL AS THE ASSOCIATED CHEMICAL CONVERSION REACTIONS.[12] 9
TABLE 2.2 SECONDARY RAW MATERIAL GROUPS FOR MANUFACTURING OF CEMENT CLINKER.[24] 13
TABLE 2.3: SCALE OF THE RANDOM, COLLECTIVE AND FINAL SAMPLES IN RELATION TO THE SCALE OF THE SHIPMENT.[34] 17
TABLE 2.4: LIMIT VALUES FOR SUBSTITUTE FUELS WHEN USED IN PLANTS FOR CEMENT PRODUCTION.[53] 39
TABLE 2.5: LIMIT VALUES OF CD AND HG FOR THE SUBSTITUTE FUELS SEWAGE SLUDGE AND PAPER FIBRE RESIDUES WHEN USED IN PLANTS FOR CEMENT PRODUCTION. 39
TABLE 2.6: SUBSTITUTE RAW MATERIALS THAT ARE USED IN PLANTS FOR THE PRODUCTION OF CEMENT CLINKER MUST COMPLY WITH THE FOLLOWING LIMIT VALUES. [57] 40
TABLE 2.7: PRECAUTIONARY GUIDE OF HEAVY METALS VALUES IN CEMENT.[57] 40
TABLE 3.1: SUBSTITUTE RAW MATERIALS USED IN THE PLANT WIETERSDORF, ASSIGNED TO THE CORRESPONDING ELEMENT GROUP. 42
TABLE 3.2: SUBSTITUTE FUELS USED IN THE PLANT WIETERSDORF WITH A SHORT DESCRIPTION OF THE FUEL 43
TABLE 3.3: MILLING TIMES OF THE DIFFERENT MATERIALS. 47
TABLE 3.4: SAMPLE TYPE, SAMPLE PERIOD, NUMBER OF SAMPLES AND ANALYSES OF THE PROCESS SAMPLES. 49
TABLE 3.5 SHOWS THE WEIGHT, WEIGHTS OF THE CHEMICALS ADDED AND THE CALCULATED CHEMICAL CONCENTRATION OF K_2O, CL, NA_2O AND SO_3 FOR THE BLIND AND MIXED SAMPLES OF EACH PROCESS SAMPLE. 51
TABLE 3.6 SHOWS THE WEIGHT, WEIGHTS OF THE CHEMICALS ADDED FOR THE GRINDING TEST SAMPLES. 52
TABLE 3.7 SHOWS THE CHEMICALS ADDED AND THE CALCULATED CHEMICAL CONCENTRATION OF K_2O AND NA_2O FOR THE GRINDING TEST SAMPLES. 53
TABLE 3.8: USED GRINDING TIMES DEPENDING ON THE PROCESS SAMPLES. 54
TABLE 3.9: SPECTROMETER SETTING OF THE AXIOS MAX AND ZETIUM X-RAY FLUORESCENCE ANALYSER. 55
TABLE 3.10: SET MEASUREMENT PARAMETERS OF THE VARIAN VISTA AX CCD SIMULTANEOUS ICP-OES. 55
TABLE 3.11: MINIMUM AND MAXIMUM INTEGRATION TIMES FOR LOW AND HIGH SULPHUR CONTENT AND FOR CARBON OF THE CSA. 56
TABLE 4.1: INPUT PER HOUR AND PERCENTAGE DISTRIBUTION OF THE FUELS USED. 60
TABLE 4.2: MATERIALS, VARIANTS FOR SAMPLE PREPARATION AND METHODS FOR ANALYSIS AND ANALYTES OF THE ROUND ROBIN TEST.[72] 66
TABLE 4.3 SHOWS THE RELATIVE STANDARD DEVIATION OF THE CONTROL TESTS BY THE REFERENCE LABORATORIES AND THE RESULTS OF THE STABILITY TESTING. A RELATIVE STANDARD DEVIATION BELOW 15 % IS MARKED AS 'X'. IF NO STANDARD DEVIATION COULD BE CALCULATED, IT IS MARKED WITH '-'. WAS THE DIFFERENCE FOR THE STABILITY TESTING LOWER THAN 15 % IT IS MARKED WITH 'XX'. 68
TABLE 4.4: CORRELATION FACTORS OF THE INDIVIDUAL CALIBRATION LINES FOR BYPASS DUST, RAW STONE (LIMESTONE + MARL), KILN INLET, HOT MEAL AND CLINKER FOR POTASSIUM (K), SODIUM (NA), SULPHUR (SO3) AND CHLORIDE (CL) WITH AND WITHOUT THE NEWLY PRODUCED MIXED SAMPLES (MS). THE MEANING OF THE ABBREVIATIONS IS AS FOLLOWS: D... VALUE OF INTERCEPT; E ... SLOPE FOR CALIBRATION LINE; RMS... STANDARD DEVIATION; RE... RELATIVE ERROR; K... K FACTOR (CONSTANT). F... QUADRATIC TERM OF THE CALIBRATION LINE IS FIXED AT ZERO AND IS THEREFORE NOT GIVEN IN TABLE. 74
TABLE 4.5: RESULTS OF THE K_2O REFERENCE ANALYSIS USING ICP-OES FOR THE BYPASS DUST REFERENCE SAMPLE (STANDARD 14) AT TWO DIFFERENT EXECUTION TIMES. 79

Table 4.6: Chemicals used, calculated K_2O values and analysed K_2O values at different grinding times for the mixed samples of bypass dust. 80
Table 4.7: Chemicals used, calculated K_2O values and analysed K_2O values at different grinding times for the mixed samples of limestone, marl, kiln inlet, hot meal and clinker. 80
Table 0.1: Notation an nomenclature of major cement compounds. [76] XIII
Table 0.2: Cement types and their composition according to DIN EN 197-1 [wt-%] [77] XIV
Table 0.3: Average chemistry of the input material for clinker production. XV
Table 0.4: shows the weight, weights of the chemicals added and the calculated chemical concentration of K_2O, Cl, Na_2O and SO_3 for the blind and mixed samples of clinker XVI
Table 0.5: Na2O-content of the fuels and the used recipe for the calculation of the fuel chemistry. XVIII
Table 0.6 shows the fuels recipe, the recipe weighted and the recipe of ‘clinker + bypass dust from the fuels’ material flow. XVIII
Table 0.7 shows the recipe for cement and the Ca-content of the materials used. XXII

List of Abbreviations

°	Degree
°C	Degree Celsius
µg	Microgram
µm	Micrometre
µS	Microsiemens
σ	Standard deviation
3D	Three-dimensional
A	Additives
Al	Aluminium
Al_2O_3	Aluminium oxide
$AgNO_3$	Silver nitrate
approx.	Approximately
AR	Alumina ratio
As	Arsenic
AWI	Approved Work Item
BP	Reference sample (Blindprobe)
BPS	Bypass dust (Bypassstaub)
Br	Bromine
C	Carbon
C_2S	Dicalcium silicate
C_3S	Tricalcium silicate
C_3A	Tricalcium aluminate
C_4AF	Tetracalcium aluminate ferrite
Ca	Calcium
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
Cd	Cadmium
CEM-I	Portland cement
CEM-V	Composite cement
Cl	Chloride
CM	Correction materials
cm^2	Square centimetre
Co	Cobalt
CO_2	Carbon dioxide
COM-CAT	Combustion catalyst
cps	Counts per second
Cr	Chromium
CSA	Carbon-Sulphur-Analyser
Cu	Copper
d	Day
D	Intercept of the calibration curve
DM	Dry matter
E	Slope of the calibration curve
e.g.	Exempli gratia (= for example)
EN	European Standard
etc.	Et cetera
EU	European Union
F	Fluorine; Fuels
Fe	Iron
Fe_2O_3	Iron oxide
FeOOH	Iron hydroxide
FeS_2	Pyrite/Marcasite
g	Gram
GmbH	Private limited company (Gesellschaft mit beschränkter Haftung)
h	Hour
H	Hydrogen
H_2O	Water
H_3PO_4	Phosphoric acid
HCl	hydrochloric acid
HF	Hydrofluoric acid
Hg	Mercury
HM	Hot meal
HNO_3	Nitric acid
hPa	Hectopascal
ICP-OES	Optical emission spectroscopy with inductively coupled plasma
i.e.	Id est (= that is)
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
J	Joule
K	Potassium

K_2O	Potassium oxide
K_2SO_4	Potassium sulphate
KCl	Potassium chloride
kcps	Kilo counts per second
kg	Kilogram
$KHSO_4$	Potassium bisulphate
KLI	Clinker (Klinker)
kN	Kilonewton
KOH	Potassium hydroxide
KS	Limestone (Kalkstein)
kV	Kilovolts
kW	Kilowatt
l	Litre
LCRM	LECO Certified Reference Material
LIMS	Laboratory Information Management System
LOI	Loss on ignition
LSF	Lime saturation factor
m	Metre
mA	Milliamperes
ME	Marl (Mergel)
mg	Milligram
Mg	Magnesium
MgO	Magnesium oxide
min	Minute
MJ	Megajoule
ml	Millilitre
mm	Millimetre
Mn	Manganese
MnO	Manganese(II) oxide
Mo	Molybdenum
MS	Mixed sample
n	Number of analyses
Na	Sodium
Na_2O	Sodium oxide
Na_2SO_4	Sodium sulphate
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NF	Normal factor
Ni	Nickel
nm	Nanometre
NP	Nepal
OE	Kiln inlet (Ofeneinlass)
ÖNORM	Austrian Standard
P	Phosphorus
P_2O_5	Phosphorus pentoxide
Pa	Pascal
Pb	Lead
RE	Relative error
REA	Flue gas desulfurization plant (Rauchgas-Entschwefelungs-Anlage)
RM	Raw meal
RMS	Root mean square error
rpm	Rotation per minute
s	Second
S	Sulphur
Sb	Antimony
SD	Sulphatisation degree
SF	Secondary Fuels
Si	Silicon
Sn	Tin
SiO_2	Silicon dioxide
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SOLR	Supplier
SR	Silica ratio; Solidification regulators
SRF	Solid recovered fuel
SRM	Secondary raw materials
t	Ton
Ti	Titanium
TiO2	Titanium dioxide
Tl	Thallium
TOC	Total organic carbon
TS	Technical spezification
U	Uranium
V	Volume; Vanadium
VOC	Volatile organic compound
W	Watt
w&p	Wietersdorf & Peggau
WIO	Waste Incineration Ordinance

WMA	Waste Management Act
WO_3	Tungsten trioxide
wt%	percent by weight
$\bar{x}$	Arithmetic mean
x_i	Concentration of the i^{th} sample
XRD	X-ray diffraction
XRF	X-ray fluorescens analysis

$\bar{y}$	Mean of the measured values y_i
y_i	Measured value of the i^{th} sample
$\hat{y}_i$	Measured value of the concentration x_i calculated using the calibration function
Zn	Zinc

1 Introduction

Since the beginning of industrialization, the proportion of CO_2 in the atmosphere has increased by around 45%. This human-made increase in greenhouse gas concentration is increasing the average temperature of our planet, commonly known as climate change. Since industrialization, the earth has warmed by around 1 °C. If the CO_2 emissions remain the same, the warming will likely rise to over 3 °C by 2100 and thus exceed the critical limit of 2 °C. [1] In order to counteract climate change, the EU has committed itself to becoming climate neutral or CO_2 neutral by 2050.[2]

This political demand is of great importance for the manufacturing industry, especially the cement industry. Cement is a hydraulic binding agent and is used as an essential component in the production of concrete. The most important process in cement production is the energy-intensive burning process of the clinker. The clinker produced is then ground to cement with gypsum as a setting regulator and selected additives, depending on the type of cement.[3] Due to the deacidification of the carbonate-containing raw material such as limestone and marl and the high energy intensity of the firing and grinding processes, 5-6 % of the global CO_2 emissions are attributed to the cement industry. A volume of 5.2 million tons of cement was produced across Austria in 2018. The specific CO_2 emissions were 521 kilograms per ton of cement.[4] Worldwide, around 3300 million tons of CO_2 were emitted in 2017 through the production of approximately 4650 tons of cement.[5] As a CO_2 driver, the cement industry has been taking intensive efforts to make cement production lower in CO_2 for years.

In recent years, CO_2 emissions in the European cement industry have been continuously reduced through the following optimization of the clinker production process:

Use of substitute fuels: Fossil fuels have largely been replaced by alternative fuels - for example plastics, paper fibre residues or sewage sludge. In 2018, the ratio of alternative fuels of the total fuel energy used in Austrian cement production was around 81 %. Due to the lower CO_2 emission factor based on the energy content of the substitute fuels compared to fossil fuels, especially coal, the CO_2 release was significantly reduced with the same energy utilization. The reason for this is a lower calorific value-related carbon content and a biogenic ratio of carbon in some substitute fuels.[6] However, fuel utilization only covers around 35-40 % of the total CO_2 emissions from cement production. A significantly higher proportion of 60-65 % of the process emissions [7] arise during the deacidification of the carbonate-containing raw material, which leads to the next optimization step.

Use of substitute raw materials: By-products and waste from other industrial production processes are used as substitute raw materials. These materials replace the natural lime, silicon, iron and aluminium raw materials, which are essential components in cement production. By-products which have already been calcined are preferably used. A large part of the CO_2 emissions that arise in the clinker burning process through deacidification of the raw materials are reduced. A large number of substitute raw materials - for example fly ash and kettle ash, broken concrete, mill scale - can be used for the manufacturing process. In 2018, about 765,918 tons of substitute raw materials were used for clinker production across Austria. This corresponds to a raw meal content of 14 %. For comparison: the European average share of substitute raw materials was only 3.6 % in 2018.[3]

Production of composite cements: Another measure to reduce CO_2 emissions is to lower the clinker/cement factor. The clinker/cement factor reflects the clinker content in the finished product cement. This means that with a lower clinker/cement factor, less clinker has to be used for the same production volume of cement. The clinker/cement factor can be reduced by adding additional materials - for example limestone, blast furnace slag or fly ash - during cement grinding. A prerequisite for extensive replacement of clinker is the use of additives that have (latent) hydraulic or pozzolanic properties. Inert additives (limestone) can also be used to a lesser extent. The average clinker content of Austrian cements in 2018 was 69.6 %, which is one of the lowest clinker contents in Europe.[3]

The realisation of the reduction of CO_2 emissions and thus innovative processes is driven by the continuous increase in prices for CO_2 certificates in European emissions trading. One certificate entitles the company to emit 1 ton of CO_2. As of January 2021, the European emission price of one ton of CO_2 was around 25 euros. The forecast is, due to the decision of the EU to be climate neutral by 2050, that the CO_2 price will gradually increase up to 55 euros per ton in 2025.[8] Therefore, it is also economically necessary for the cement industry to minimize CO_2 emissions.

Due to the increasing use of substitute fuels and substitute raw materials, as well as the increasing use of additives, cement manufacturers are faced with challenges of different nature:

Firstly, the legal aspects for cement production must be taken into account. The necessary regulations and quality criteria of the substitute fuels and substitute raw materials can be found in the Waste Incineration Ordinance and the Waste Management Act, or in the "Technical Principles for the Use of Waste as Substitute Raw Materials in Cement Production Plants". On one hand, the focus is on compliance with the heavy metal content in the substitute fuels and substitute raw materials used, whose limit values are specified by law, and on the other hand the limit values of the heavy metal content in the end product cement, which are to be understood as precautionary guide values in the “Technical Principles”. In order to ensure that the limit values in the cement produced are not exceeded, the heavy metals from substitute fuels and substitute raw materials as well as from the additives have to be quantified.

Another point are the chemical and mineralogical aspects. For optimal cement properties, the mineralogy of the clinker must follow certain specifications. The mineralogy of the clinker is influenced by the chemistry of the raw meal, the chemistry of the fuels used and the process design and management. Substitute raw materials have a directly measurable influence on the raw meal composition. This raw meal chemistry is shifted by the ashes of fossil fuels and substitute fuels. In order to set the prerequisites for good mineralogical properties of the clinker, a plant-specific ratio of CaO, SiO_2, Al_2O_3 and Fe_2O_3 must exist in the composition of the raw meal and thus also in the clinker. In addition, certain elements, e.g. phosphorus, have a negative influence on the product properties if a defined limit value is exceeded in the cement. [9], [10] Therefore, the depositions of such elements must be restricted in the clinker manufacturing process. At this point it must also be taken into account that the increased use of additives also introduces "undesired" elements.

Furthermore, with regard to the procedural aspects, it must be taken into account that the increased use of substitute fuels and substitute raw materials entails a general increase in the amount of alkaline input. The high sintering temperature of the clinker together with high alkali contents favours the formation of alkali cycles in the kiln and leads to the formation of rings and balls in the kiln if unsuitable countermeasures are taken. By interrupting the flow of material and air, a clinker of inferior quality is produced and in the event that the deposits do not come off during the ongoing process, the kiln has to be shut down and mechanically cleaned. When the kiln is cleaned, the refractory lining can be damaged. In addition, a temperature change in the rotary kiln due to the shutdown leads to severe material wear and thus to high maintenance costs.

Not to be forgotten are the economic aspects related to process complications. A process standstill due to a process disruption in the rotary kiln always means a loss of production, regardless of the other maintenance costs. With clinker costs of approximately 40 €/t and a kiln output of 100 t/h, this is approximately 4,000 €/h due to the production stoppage. The cleaning time of the kiln depends on the hardness and diameter of the attachments, but in any case, requires several hours. Furthermore, legal consequences of a financial nature must be taken into account in economic terms, if the normative limit values for heavy metals in cement or emissions are exceeded. Customer complaints due to changed product properties must not be disregarded and can lead to high claims for damage.

The high complexity of the effects and the interaction of the different manipulated variables requires a scientific treatment of the topic and also the underlying analytics as a basis for assessment. The aim of this work is the consideration or assessment of the entire process chain and the development of tools for the targeted assessment of the effects of multiple process changes through substitute fuels, substitute raw materials and the increased use of additives.

For this purpose, the following chapter, *State of the art*, explains the cement production process and the analysis methods for quality assurance of the raw materials, fuels, intermediate and end products. In addition, the sampling and sample preparation procedures for substitute fuels and substitute raw materials are explained. For this a distinction is made between qualified random samples and samples for process monitoring, also a compact description of the legal aspects and an insight into the process technology is made. To this end, the individual challenges - raw meal specification, process influence on kiln operation with an eye on alkali cycles and their management and legal aspects of cement production - are examined more closely.

The *Experimental part* describes the materials used specifically in the ‘Wietersdorf’ cement plant and the analyses carried out to record the chemical composition and heavy metal content of the samples.

The chapter *Evaluation* explains the assessment tools developed, in this case the development of an all-encompassing material flow balance. Therefore, the development and its theoretical calculation is explained. The chemical focus for the development of the mass balance is on the renewal of the analysis with regard to alkali, chloride and sulphur detection by means of X-ray fluorescence analysis (XRF), and its problems, i.e. the matrix effects, which is also considered in the evaluation. Another point that this thesis includes is the round robin test on the applicability of X-ray fluorescence analysis as an alternative method to optical emission spectroscopy with inductively coupled plasma (ICP-OES) for solid recovered fuels.

2 State of the art

2.1 Cement production process

Cement is largely made from the raw materials limestone, marl and their natural mixture of grey limestone (limestone marl).[11] Correction materials such as quartzite and mill scale are used to a lesser extent in order to obtain the desired silicon and iron content. As part of this master's thesis, the cement manufacturing process is described using the example of the Wietersdorf plant and its specifications, because of the cooperation with the company "w&p Zement".

The necessary raw materials are extracted in quarries. For economic reasons (e.g., transport costs), the production usually takes place in the immediate vicinity of the raw material deposits.[12] This allows the raw materials, after they have been crushed in the primary crusher, to be transported to the cement plant by conveyor belts. In the so-called raw stone store, the raw materials are temporarily stored, separated according to lime and clay content. The proportions of the main raw materials for cement production are on average one part limestone and two parts clay or marl.[13]

For economic and ecological reasons, natural primary raw materials are replaced by substitute raw materials according to requirements. Secondary raw materials have been used for clinker production for years.[14][15] In the Wietersdorf plant, rust and fly ash from various companies in the immediate vicinity are predominantly used. The substitute raw materials used are discussed in more detail in *section 3.1.2.* The amount of substitute raw materials used depends on the availability and the technical, legal and economic framework.

Basically, the manufacturing process of clinker consists of the preparation of the raw material to be burned and the burning process. In Austria, clinker is produced almost exclusively using the dry process. In addition to the dry process, there are three other processes with a higher moisture content, but these wet and semi-wet processes are now a thing of the past in cement production, as these are no longer justifiable from an economic and ecological point of view. The dry process is also used in cement production at the Wietersdorf plant. A rotary kiln with multi-stage cyclone preheaters and calciner as well as a bypass gas system is used. This process system is examined in more detail in this work. *Figure 2.1* gives an overview of cement production using the dry process at the Wietersdorf plant.

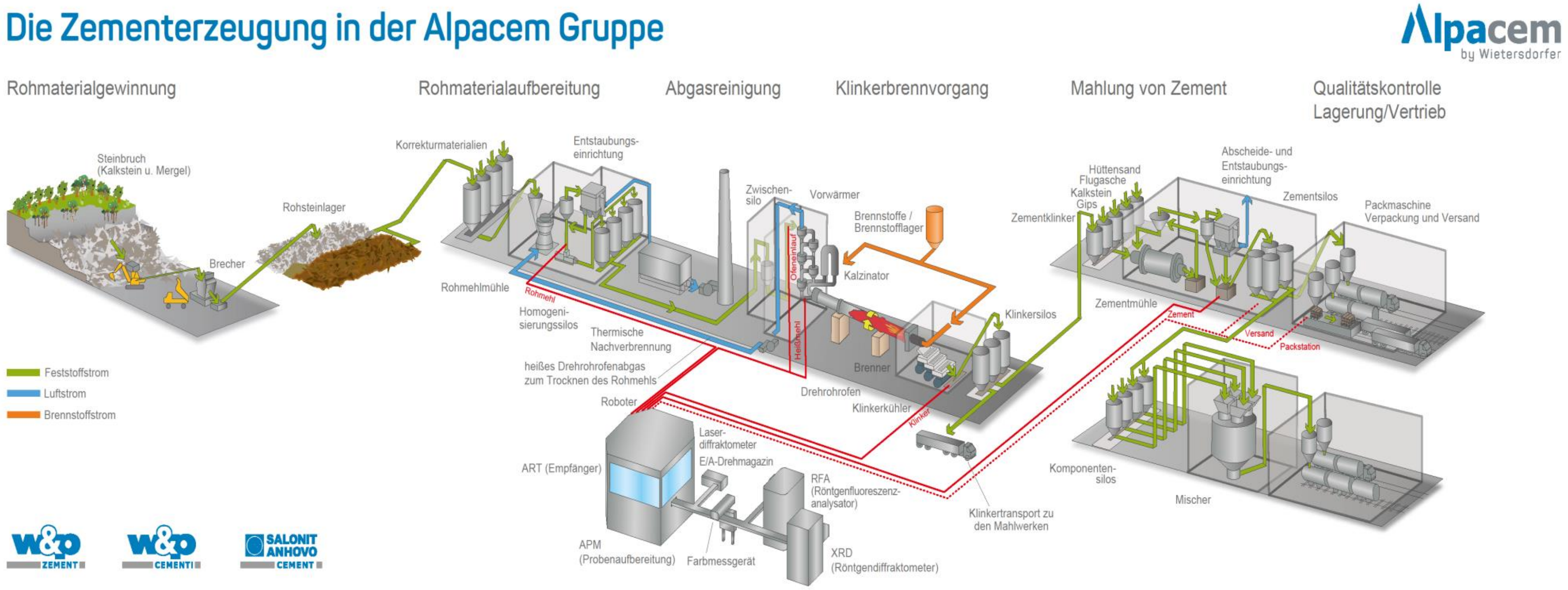


Figure 2.1: Flow chart of the cement production at the Wietersdorf plant using the dry process.

Dry raw meal is generated during the grinding process in the raw meal mill by the hot kiln exhaust gases, which are passed through the entire process system.[12][16] Usually, the raw meal is homogenized in silos, stored in an intermediate silo and kept ready for the burning process. However, there are no large homogenization silos or blending beds at the Wietersdorf plant. This makes the mixing ratio of the substances used in the raw mill and thus the correct chemical composition of the raw meal, despite a high and very variable proportion of substitute raw materials, all the more important. Correction materials such as mill scale or fine ore are often necessary to achieve the optimal composition for clinker production.[12][18] The range for the optimal composition of the raw meal is small, as can be seen from the three-component diagram CaO - Al_2O_3 - SiO_2 in *figure 2.2*. To simplify the assessment of the chemical composition of the raw meal, as well as for clinker and cement, the control variables lime saturation factor, silica ratio and alumina ratio are used.

The lime saturation factor (LSF) gives the actual percentage of CaO, which can be combined with SiO_2, Al_2O_3 and Fe_2O_3 to form the clinker phases, which are explained shortly below. The lime saturation factor should be in the range of 101-103 % for raw meal and in the range of 92-98 % for a satisfactory clinker quality. The LSF is calculated using the equation 2.1 [17]:

$$LSF\ [\%] = \frac{100*CaO}{2{,}8*SiO_2+1{,}18*Al_2O_3+0{,}65*Fe_2O_3} \qquad (2.1)$$

The silica ratio (SR) is a guiding value that describes the proportion of silica phases to aluminate and ferrite phases. Therefore, this value provides information about the amount of Al_2O_3 and Fe_2O_3 that is present in the melt or bound in the solid silicate phases. For raw meal the silica ratio should be in the range of 2.45 – 2.65. The SR is calculated using the equation 2.2:

$$SR = \frac{SiO_2}{Al_2O_3+Fe_2O_3} \qquad (2.2)$$

The alumina ratio (AR) shows the ratio of aluminate phase and ferrite phase in the clinker. It indicates which of these phases is forming the melt phase. For raw meal the alumina ratio should be in the range of 1.50 – 1.60. The AR is calculated using the equation 2.3 [18]:

$$AR = \frac{Al_2O_3}{Fe_2O_3} \qquad (2.3)$$

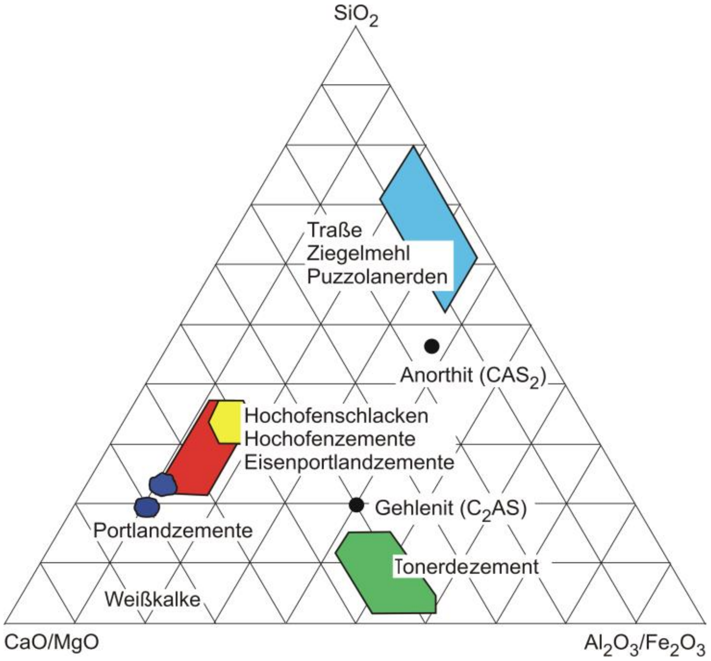


Figure 2.2: Three-component diagram CaO-SiO_2-Al_2O_3+Fe_2O_3.[12]

Before the actual burning process, the homogenized raw meal runs through the preheater, which consists of a system of 5 cyclones, through which the raw meal is fed in counter current to the kiln gases. During the passage through the five calciner stages in the preheating tower, the raw meal is heated to a temperature of 750-800 °C, with chemical reactions of the raw meal occurring in certain temperature ranges.

At 200-400 °C, the absorbed water is released from the raw meal in the calciner stage 1. In calciner stage 2 at approximately 450-600 °C, clay decomposition and the formation of metakaolinite occur. The decomposition of metakaolinite and the formation of active oxide mixtures occur at a temperature of 600-750 °C in the calciner stages 3 and 4. This is also where the deacidification of limestone begins in the presence of Al_2O_3 and SiO_2. The preheated raw meal from the calciner stage 4 is heated in the calciner combustion chamber and on the further way to the calciner stage 5 to about 750-800 °C, whereby the entire decarbonation process is run through. The calcined raw meal is present in cyclone stage 5. An overview of the chemical reactions that occur in the individual temperature ranges and their reaction equations are given in *table 2.1*.

Table 2.1 lists the processes that take place during cement production in the different temperature ranges, as well as the associated chemical conversion reactions.[12]

TEMPERATURE [°C]	PROCESS	CHEMICAL REACTION
20-200	Release of free water [drying]	
200-400	Release of adsorbed water	
450-600	Clay decomposition; formation of metakaolinite	$Al_4(OH)_8Si_4O_{10} \rightleftharpoons 2\ (Al_2O_3 \cdot 2\ SiO_2) + 4\ H_2O$
600-950	Decomposition of metakaolinite; formation of reactive oxide mixtures; start of limestone deacidification in the presence of Al_2O_3 + SiO_2	$Al_2O_3 \cdot 2\ SiO_2 \rightleftharpoons Al_2O_3 + 2\ SiO_2$ $CaCO_3 \rightleftharpoons CaO + CO_2$
800-1000	Limestone decomposition; simultaneous formation of calcium silicate and calcium aluminate	$CaCO_3 \rightleftharpoons CaO + CO_2$ $3\ CaO + Al_2O_3 + 2\ SiO_2 \rightleftharpoons 2\ (CaO \cdot 2\ SiO_2) + CaO \cdot Al_2O_3$
1000-1300	Melting of the raw meal; lime absorption by dicalcium silicate and tricalcium aluminate; formation of tetracalcium aluminate ferrite	$CaO + SiO_2 \rightleftharpoons CaO \cdot 2\ SiO_2$ $2\ CaO + SiO_2 \rightleftharpoons 2\ CaO \cdot SiO_2$ $2\ CaO + CaO \cdot Al_2O_3 \rightleftharpoons 3\ CaO \cdot Al_2O_3$ $3\ CaO + CaO \cdot Al_2O_3 + Fe_2O_3 \rightleftharpoons 4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$
1200-1450	Further calcium absorption by tricalcium silicate	$CaO + 2\ CaO \cdot SiO_2 \rightleftharpoons 3\ CaO \cdot SiO_2$

The calciner is used for improved calcination of the raw meal, which already takes place in the preheating tower, as mentioned before. The main advantage of the calciner is that the secondary firing at 900 °C generates enough energy to achieve complete decarbonization of the raw meal. Therefore, the dissociation of the carbonate content of the raw meal is complete before it enters the rotary kiln. For the secondary firing lower quality fuels can be used too. In addition, the process step is outsourced from the rotary kiln through the precalcination of the raw meal in the calciner, so that the mineralogically decisive melting phase formation of the raw meal in the rotary kiln can be achieved after a shorter distance. Therefore, a higher clinker throughput is achieved with a given kiln dimension.[12] A residual deacidification of less than 10 % takes place in the rotary kiln if the preheating system is equipped with a calciner. Without the calciner, this residual deacidification in the rotary kiln is about 50-60 %.[19]

After deacidification in the preheater system, the material enters the rotary kiln. As the kiln rotates, the material takes on a spherical shape (granules) and, due to the inclined position of the kiln pipe (2° - 4°), it reaches increasingly hotter kiln zones in the direction of the burner. The entire fuel energy required to burn the cement clinker is divided between the primary firing in the rotary kiln and the secondary firing on the calciner. At material temperatures of around 1450 °C, the clinker minerals are formed through the sintering process. The resulting clinker phases include tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminate ferrite (C_4AF). The clinker phases are hydraulically active, which means that these phases allow the cement to solidify by binding water. The phases C_3S and C_2S are particularly important for the strength development of the cement. C_3S causes a rapid initial hardening of the cement while giving off a high heat of hydration. Heat of hydration is the warming that occurs when the cement reacts with water (hydration). Phase C_2S is responsible for a slow increase in strength, but a higher final strength of the cement with increasing age. The released heat of hydration is only about half that of C_3S. The clinker phase C_3A causes an increase in early strength in larger quantities, which is associated with a very high heat of hydration. The initial hardening can be regulated by adding sulphate carriers such as gypsum. Phase C_4AF hardens relatively slowly, influences the colour of the cement due to stored magnesium ions and is useful for controlling cement production.[11] The used cement notation of the individual phases is attached in the *appendix i.*

After the sintering process, the clinker granules fall onto the grate of the clinker cooler, at the kiln outlet. Rapid cooling is necessary in order to maintain the hydraulic properties of the clinker. Otherwise, slow cooling can lead to a reverse reaction of the C_3S phase, which is formed in the sintering process through the additional incorporation of SiO_2 into the C_2S phase, as the C_3S phase decomposes into the C_2S phase and CaO below 1250 °C.[20] Most of the hot exhaust air that is produced during cooling is fed directly into the kiln and used during the firing process. The clinker cooler exhaust air is dedusted in a filter.[21]

For the firing process at the Wietersdorf plant, a rotary kiln with a kiln length of 58 m, a gradient of 2° and a rotational speed of 0.2 - 4 rpm is used. This achieves a clinker production output of 91.7 t/h or 2200 t/d.

The finished cement is a mixture of finely ground clinker, additive (limestone, slag, fly ash) and solidification regulator (sulphate carriers, such as gypsum). The additives and solidification regulators are examined in more detail in *sections 2.2.4 and 2.2.5*.

The materials needed for cement grinding, the crushed cement clinker, additives and solidification regulators, are temporarily stored in silos. Depending on the type of cement required, the cement clinker is mixed with the required additives in accordance with the cement standard EN 197-1, which are attached in the *appendix i,* and then ground in the cement mills. At the Wietersdorf plant, two ball mills with a capacity of 35 t/h and 70 t/h are used. The grinding fineness of the cement influences the physical and cement-technological properties of the end product and the grinding fineness is determined by the type and duration of the grinding process. Most cement mills, as in Wietersdorf, work in combination with adjustable air classifiers, which separate the cement with the required fineness from the ground material.

The Blaine value (specific surface area) defines the grinding fineness and is for cement generally 3000 - 5000 cm^2/g. In principle, the following applies: the larger the specific surface, the faster the reaction with water takes place, the higher the hydration heat during hardening and the faster the strength develops.[12][21] The ground cement is stored in Versa-silos for filling in trucks or packed in bags in the packing station.

Ongoing process controls are carried out to ensure the quality of the intermediate and end products and to control the process. The chemical and mineralogical composition as well as the heavy metal content of the raw materials, intermediate and end products are analysed. The analytical equipment and methods used for this are examined in more detail in the *section 3.2*.

2.2 Description of the input materials

2.2.1 Raw materials

The main components required for the raw material mixture are calcium oxide (CaO) and silicon dioxide (SiO_2) and, to a lesser extent, aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3). The rocks that contain the most important main components for the clinker burning process are limestone, clay and their naturally occurring mixture, marl.

- Limestone:

  Limestone is a naturally occurring mineral that consists principally of calcium carbonate $CaCO_3$. Many limestones are remarkably pure, with less than 5 % of non-carbonate impurities. Limestone is found in many forms and is classified in terms of its origin, chemical composition, structure, and geological formation. It occurs widely throughout the world, and is an essential raw material for many industries.

  On the basis of the global production of cement, the limestone used in its production probably amounts to about 1500 million t/a, or one third of the total extracted.

  The colour of limestone often reflects the levels and nature of the impurities present. White deposits are generally of high purity. Various shades of grey and dark hues are usually caused by carbonaceous material and or iron sulphide. Yellow, cream and red hues are indicative of iron and manganese.[22]

- Clay:
  Essential components in clay deposits are the very fine-grained clay minerals and, in small amounts, quartz and feldspars. Clay minerals and feldspar are compounds that are essentially composed of silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and the alkali oxides (K_2O) and (Na_2O). The quartz consists exclusively of silicon dioxide (SiO_2). Iron oxide (Fe_2O_3) is found in clay as a component of the clay minerals or as iron hydroxide (FeOOH) and partly also as pyrite or marcasite (FeS_2). [23]

- Marl:
  Marl is a sedimentary rock that consists mainly of limestone and clay. It can also contain coarser material such as silt and sand. Depending on the composition, one speaks of lime marl (high proportion of lime) or clay marl (high proportion of clay).

2.2.2 Substitute raw materials

In addition to natural raw materials, secondary raw materials are used in increasing amount. These are predominantly waste materials or by-products from other industrial production processes that can be recycled in the clinker burning process or in the cement manufacturing process, such as limestone sludge, used foundry sands and fly ash. They also contain silicon dioxide, aluminium oxide, iron oxide and/or calcium oxide as main components and are combined with the raw materials in such a way that the requirements for the specified clinker composition are met with homogeneous processing.

Secondary raw materials can be classified into different groups depending on their chemical composition, which are identified by the chemical element that this secondary raw material contains to a significant extent and that predominates in the composition of the raw material mixture. Accordingly, the alternative raw materials can be divided into, for example, Ca, Si, Fe, Si/Al, Si/Al/Fe/Ca, S and F group, as shown in *table 2.2*.

In 2018, the Austrian cement industry used 765,918 tons of these alternative raw materials for clinker production. Their ratio in the raw meal produced was thus 14 %. That is a significantly higher value than is customary internationally. In Europe, the content of alternative raw materials was 3.6 %.[3]

Table 2.2 Secondary raw material groups for manufacturing of cement clinker.[24]

GROUP	NATURAL MATERIALS	SECONDARY RAW MATERIALS
Ca	Limestone	Lime sludge Lime burning waste Calcium fluoride Waste from stone cutting Aerated concrete granulates
Si	sand	Waste foundry sand Oil contaminated soils Old sands Sand trap residues Sands from floor washing systems Road break Refractory outbreak
Fe	iron ore	Gravel burn Contaminated ore Red mud Stell mill dust Mill scale
Si-Al	clay	Bentonite Fuller's earth
Si-Al-Fe-Ca	marl	Fly ash Ashes from the paper industry Rust ashes Slag Broken concrete
S-	gypsum	REA gypsum, chemical gypsum
F		CaF_2- filter sludge

2.2.3 Correction materials

Depending on the raw material situation at the location of the cement plant, it may be necessary to add pure limestone, iron ore, sand or other corrective substances like mill scale or quartzite to the raw material mixture in order to meet the raw meal specifications. Using the example of normal raw meal from the Wietersdorf plant, the raw meal specifications LSF = 101, SR = 2.55 and AR = 1.55 must be met. This specification of the raw meal is used specifically for the Wietersdorf plant, as the fuel mix used has already been taken into account, so that a good clinker quality is obtained.

In addition to natural raw materials such as quartzite, alternative raw materials such as lime sludge, used foundry sands and fly ash can be used as correction materials. They also contain silicon dioxide, aluminium oxide, iron oxide and/or calcium oxide as main constituents (as mentioned before in *section 2.2.2*) and are combined with the raw materials in such a way that the requirements for the specified clinker composition are met.[25]

2.2.4 Cement Additives

The addition of various fillers and additives, which are by-products from other large-scale processes (e.g. slag or fly ash), in the grinding step has the advantage that the clinker content of cement products can be reduced. The clinker content in the finished cement is assessed using the clinker/cement factor. The cement properties can be changed depending on the type of additive and the amount used. Therefore, the different types of cement must be characterized according to their composition. For the characterization, the clinker/cement factor is also included. For example, a CEM-I cement has a clinker content of 91-96 %, whereas a CEM-V composite cement is produced with 20-64 % of clinker.[6]

The basic prerequisite for the possible reduction of the clinker content in the cement is that the additives, in addition to the clinker, also have hydraulic properties for hardening the cement. The individual ingredients can be classified according to the characteristics of the hydraulic properties (hydraulic, latent-hydraulic, pozzolanic and inert).

If hydraulic substances (e.g. burnt oil shale) come into contact with water, they develop their hydraulic effect without further stimulation. Latent hydraulic substances (e.g. blast furnace slag), on the other hand, must be stimulated in addition to contact with water in order to develop the hydraulic properties. In order to maintain the strength-building effect of pozzolanic substances (e.g. trass or high-silica fly ash), reactive silica and calcium oxides have to be present. The pozzolanic substances react with calcium hydroxide to form C-S-H phases in order to achieve their strengthening. The inert substances (e.g. ground limestone) have no hydraulic or pozzolanic properties.[26][27]

The use of additives achieves environmental benefits such as reducing energy consumption, reducing CO_2 emissions into the air, conserving natural resources and avoiding landfills. It is also used to control the properties of the cement and to reduce the cost of cement production. In Europe, the average content of additives in cement is currently 15-20 %.[28]

2.2.5 Solidification regulators

Sulphate carriers such as gypsum and natural anhydrite are added as solidification regulators during cement grinding in order to regulate the solidification time of the cement. Without these sulphate carriers, the freshly made cement paste would solidify immediately, since the C_3A component is not bound as trisulphate ($C_6AS_3H_{32}$) and tetracalcium (C_4AF), aluminate hydrate crystals would result immediately, see equation 2.4.

$$2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8 \tag{2.4}$$

A sulphate deficiency can also lead to rapid solidification, as the trisulphate converts to monosulphate (C_4ASH_{12}) before the main reaction of the tricalcium silicate, as seen in equation 2.5.

$$C_6A\bar{S}_3H_{32} + 2\ C_3A\ +\ 4H_2O \rightarrow 3C_4\bar{S}H_{12} \qquad (2.5)$$

The sulphate carriers are distinguished between anhydrite ($CaSO_4$), hemihydrate ($CaSO_4$*1/2 H_2O) and dihydrate ($CaSO_4$*2H_2O). The modifications of the sulphate carriers differ in their effect on the set retardation of the cement due to the different water solubilities. Adding hemihydrate will shorten the time it takes to form trisulphate in comparison to dihydrate. Since the formation of trisulphate increases the solidification time of the cement, it is shortened by adding hemihydrate. But, with the use of dihydrate, a higher total heat is developed during hydration. [29]

A mixture of anhydrite and dihydrate is beneficial for cement production. In the Wietersdorf plant, natural gypsum is used as anhydrite and REA gypsum as dihydrate.

2.2.6 Fuels

The traditional fuels in the cement industry have been hard coal and lignite since the mid-1970s, and to a lesser extent also heavy heating oil. Light heating oil and gas are also used to start up the furnace and for drying processes. Since the 1990s, a significant part of coal has been replaced by petroleum coke. Petroleum coke is a coal-like fraction of mineral oil that is obtained during crude oil processing. [23]

Metals and mineral components are brought into the burning process by fuels. The composition of the fuels, especially their ashes, must therefore be taken into account when mixing the raw meal. Essential characteristics of the fuel are the calorific value, content of volatile components and the content of ash and sulphur.

2.2.7 Alternative fuels

Different types of combustible waste are substitute fuels. Above all, used tires and oil as well as, to a lesser extent, bleaching earth, waste wood, plastic waste and processed fractions of production and commercial waste as well as household waste are used.[23][25] In particular, the ash content of these alternative fuels, the content of the main constituents of the ash and the content of alkalis, chloride and sulphur must be taken into account. Furthermore, the Zn and Pb content of substitute fuels must be taken into account, as these metals influence the properties of the clinker if more than 0.02 % of them are incorporated into the clinker.[30]

The international comparison with data from 2017 shows that Austria has the highest substitute fuel rate worldwide. In 2018, 81.2 % of the thermal energy demand in the Austrian cement works was covered by alternative fuels. In total, the domestic cement works recycled 555,614 ton of substitute fuels - for example non-recyclable plastic waste, old tires and paper fibre residues.[3]

2.3 Principles of sampling and sample preparation

2.3.1 Procedure for sampling

Sampling is the first and also the most important step in guaranteeing the sample quality and thus the informative value of the analysis data. In order to achieve the best possible result of the sampling, technically justified and standardized methods were created, which help to avoid the loss of chemical information and to minimize contamination.[31]

In the following section, the basics of the sampling of solids that are sampled in a cement plant are discussed in more detail. In principle, two types of sampling are carried out at the Wietersdorf plant. First, the sampling of bulk goods or large deliveries from a pile, such as the raw materials from mining and the substitute raw materials, substitute fuels and primary fuels that are delivered by truck. Second, the sampling from a conveyor belt, which is taken for the input materials and ongoing process samples for quality assurance and process control.

For the first type of sampling, sampling from a pile, the two big challenges were the sampling of the substitute raw materials and substitute fuels, since these substances are declared as waste and are relatively inhomogeneous.

The aim of sampling is to ensure that the sample taken is representative of the entire batch or shipment. Therefore, a sampling plan must be drawn up, before sampling can be carried out. For this, all prior information and preliminary examinations of the goods must be taken into account. In addition, it must be known which ingredients are to be examined and which problems are to be expected during sampling.

The following is specified in the sampling plan:

- Number of samples
- Type of sampling device and selection of the device for cleaning
- Sampling site
- Number and type of sample transport containers
- Requirements for sample transport
- Personal protective measures

If the plan does not completely correspond to the conditions found due to local inhomogeneities, the actual volume or abnormalities in terms of smell, taste, appearance and colour, it must be adapted on site.[32]

After completion of the sampling plan, the actual sampling can be carried out. For each qualified sample, the number of required random samples, which were previously determined, must be taken, distributed as evenly as possible, from the associated subset of the waste characterization.[33]

For bulk goods that are delivered by truck, certain sampling points are selected in order to ensure a representative sample from all parts of the shipment. For trucks up to 15 t, five extraction points are selected, as shown in the following *figure 2.3*.[34]

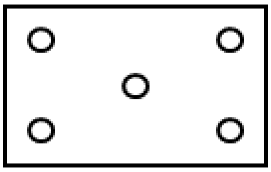


Figure 2.3: Selected extraction points (in the middle and approximately 500 mm from the sides) for bulk goods, transported in trucks up to 15 t.[34]

The randomly taken samples are mixed to form a collective sample. The final sample is generated with a sample divider. After completing the sampling, a sampling protocol must be drawn up on site.

Table 2.3 provides an overview of the required sample quantities depending on the scale of the shipment.

Table 2.3: Scale of the random, collective and final samples in relation to the scale of the shipment.[34]

SCALE OF A SHIPMENT [t]	1 - 5	5 - 500	MORE THAN 500
NUMBER OF RANDOM SAMPLES	7	2 PER TON (MAX. 20)	MAX. 40
SCALE OF SAMPLES [kg]	MAX. 1	MAX. 1	MAX. 1
SCALE OF COLLECTIVE SAMPLE [kg]	MAX. 7	MAX. 20	MAX. 40
SCALE OF FINAL SAMPLES [g]	0.5	0.5	0.5

The second type of sampling, sampling from a conveyor belt, was carried out for the input materials, like the raw materials, correction materials and solidification materials, as well as for the process materials, like raw meal, kiln inlet, hot meal, bypass dust and clinker.

In this case, individual samples were taken to check the quality and process flow. Therefore, no qualified samples were required. The sampling was carried out either manually from the stopped conveyor belt, as manual sampling from the moving conveyor belt is not permitted for safety reasons, or automatically from the running conveyor belt.

For manual sampling, according to ÖNORM EN 15442 – "Solid recovered fuels - Sampling method", a material disc; i.e. a sample over the entire width of the conveyor belt, must be taken. The length of the disc of material must be at least three times the size of the nominal sieve size of the material. [35] The drawn sample is homogenized using a paddle. A random sample is taken from the homogenized material and placed in a suitable sample container, which must be adequately labelled. The random sample must be sufficient for further sample preparation and sample analysis. The remaining sample material is returned to the conveyor belt.

2.3.2 Procedure for sample preparation

The aim of sample preparation is to reduce the amount of sample drawn to one or more test amounts in such a way that the composition of the sample is not changed during the entire sample preparation process. In addition, compliance with the requirements of the analysis method that is used must be guaranteed. The importance lies in maintaining the representativeness of each individual sub-sample based on the sample taken, which means that every particle present in the sample before the sample preparation is included with the same probability in the sub-sample remaining after the sample preparation. The methods used for this are divided into sample division and reduction of the particle size of the sample. The following devices are used to split samples or reduce the particle size:

Devices for sample division:

- Corrugated divider
- Rotary sample divider
- Shovels and sampling shovels

Devices for reducing the particle size:

- Coarse granulator or wood crusher
- Cutting mill
- Shredders

Before starting the sample preparation process, a sample preparation plan must be drawn up, just like for sampling. The relevant prior information and details of the material to be extracted, which were previously recorded, are taken into account here. As listed in section 7.2 of the ÖNORM EN 15443 – “Solid Secondary Fuels - Procedure for the Production of Laboratory Samples” [36], this information about the material to be taken must be recorded, if a secondary fuel is considered:

a) *“Minimum sample size according to the sampling plan;*
b) *actual size of the sample m_0;*
c) *nominal sieve size of the sample;*
d) *Form factor of the sample;*
e) *Particle size reduction requirements for the analysis to be performed;*

f) *required amounts of each of the particle fractions and their limitation to the methods of sample preparation. Sample preparation is the process of preparing a sample for a number of tests to be performed on that sample. Some of these tests do not require reducing the particle size or drying the material in the sample. Other tests require very small, homogenized subsamples with a small particle size. A sample preparation plan must meet all of these requirements."*[36]

For sample preparation, the plan must contain at least the following information:

- Method of reduction (sample division or reduction of the particle size)
- Description of the procedure
- Procedures and equipment used
- Mass before and after reduction
- Nominal sieve size before and after the reduction
- Form factor before and after the reduction
- Mass to be retained for analysis
- Purpose of the product of this reduction step
- Number of steps necessary to achieve the desired mass and particle size

The actual implementation of the sample preparation must be carried out in accordance with the details of the sample preparation plan. It must also be ensured that the material of the partial sample is thoroughly homogenized after each step; no material of the partial sample is lost; no components are left out and, if this is not possible, the type and mass fraction of the substance removed from the sample must be recorded; a sufficient amount of sample material is set aside for all analyses to be carried out. The partial samples, which serve as reserve samples, must be clearly labelled and stored in tightly closed containers. [36]

2.4 Analysis methods

2.4.1 Calorimeter

A combustion calorimeter measures the heat that a sample generates when it burns under controlled conditions. In the decomposition vessel, the so-called "bomb", the sample is burned with an excess of oxygen. The resulting heat is released into the environment and measured. In order to avoid disruptive external temperature influences, the system is surrounded by a casing. [37]

Principle:

A certain amount of a solid or a liquid is weighed into a crucible and placed in the bomb. The sample in the bomb is connected to the ignition wire with a cotton thread. The vessel is then filled with oxygen (30 bar) and the sample is burned. During the combustion process, the core temperature in the crucible can rise to 1000 °C. This also increases the pressure. All organic substances burn and oxidize under these conditions. The heat generated during the combustion process can now be determined. The measurement result is referred to as the calorific value.

With the double-dry calorimeter, the temperature increase in the decomposition vessel itself is measured. This is surrounded by a large casing of aluminium. The heat of combustion is thus measured directly and not transferred to the water in the inner boiler, as is the case with classic calorimeters. This methodology is mainly used in the waste management industry.[37] *Figure 2.4* shows the IKA C 7000 calorimeter and the principle of double dry analysis.

Figure 2.4: IKA C 7000 calorimeter and the principle of double dry analysis. [37]

2.4.2 CSA - Carbon-Sulphur Analyser

A carbon and sulphur analyser is used to analyse the percentage of carbon and sulphur that is present in a sample. The CSA is equipped with either a resistance furnace for the analysis of organic compounds, an induction furnace for inorganic compounds or a combination of both furnaces. The selection of the furnace (resistance furnace or induction furnace) depends on the test requirements and properties of the sample material. Carbon and sulphur are measured simultaneously with an accurate infrared detection system, with the analysis results being expressed as percentages by mass of carbon (% C) and sulphur (% S) of the sample. Using the induction furnace, a carbon content of 0.0001 % to 6 % and a sulphur content of 0.0001 % to 30 % can be measured, while using the resistance furnace, both contents can be measured from 0 to 100 %.[38]

Principle:

The sample to be examined is heated in an oxygen-rich environment to oxidize the carbon and sulphur content of the sample material. Carbon monoxide (CO), carbon dioxide (CO_2) and sulphur dioxide (SO_2) are formed in the process. The combustion gases are cleaned with a dust filter and moisture absorber and then passed through detection cells to measure the carbon and sulphur content. First the sulphur dioxide is measured in the infrared cells, consequently the oxidation of carbon monoxide to carbon dioxide and sulphur dioxide to sulphur trioxide takes place. The SO_3 gas is removed with cellulose wool and the carbon content is measured by the infrared cells. The measured data are compared with the mass of the sample to identify the content of the respective elements in the sample. The residual gas is finally released.[39][40] A flow diagram of a CSA is shown in *figure 2.5.*

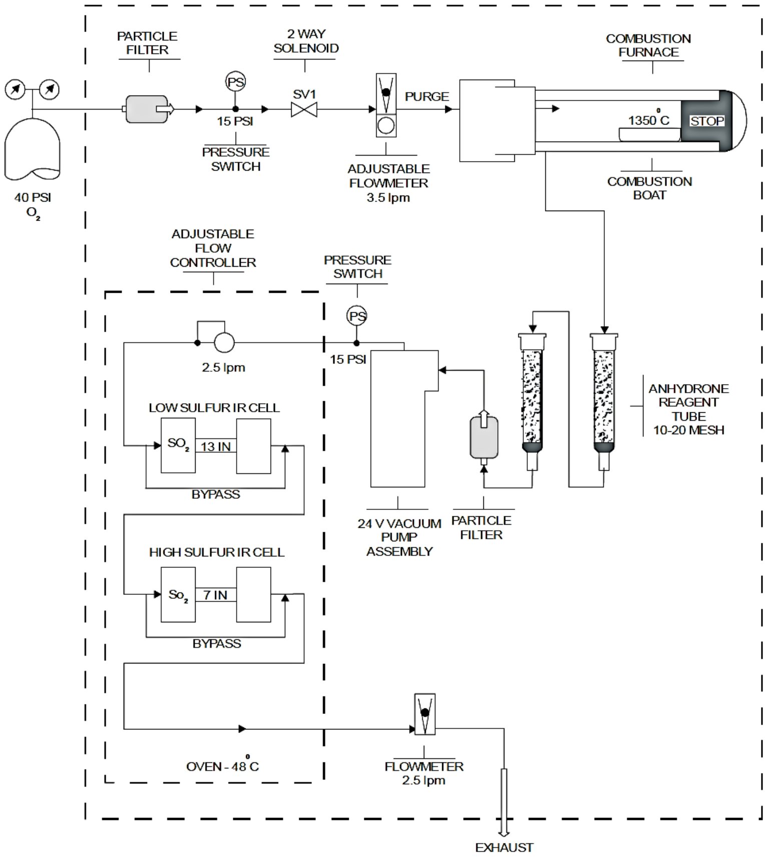


Figure 2.5: Analytical flow diagram of a carbon-sulphur-analyser CSA [41]

2.4.3 ICP-OES - Optical Emission Spectroscopy with Inductively Coupled Plasma

Optical emission spectroscopy with inductively coupled plasma (ICP-OES) is used for the analysis of elements in aqueous solutions in the concentration range mg/l to µg/l. Liquid and gas samples can be injected directly into the measuring instrument, while solid samples usually require extraction or acid digestion in order for the analytes to be in solution. The method enables the simultaneous determination of all metals and some non-metals (up to 70 elements[42]) from acidified, aqueous solutions up to a total dissolved substance content of approximately 1 g/l. ICP-OES is one of the most powerful and popular analysis tools for the determination of trace elements. However, the difficulty with this analytical method is to guarantee representative analytical results despite the strong dilution of the sample for the measurement solution. This challenge is discussed in more detail in *section 4.3* in the evaluation.

Principle:

With ICP-OES analysis, the sample solution is introduced as an aerosol into an inductively coupled argon plasma via a pneumatic atomizer system. At a temperature of around 10 000 K in the plasma, the elements are excited and ionized. When a photon is emitted, both the atomic and the ionic excited species then revert to their ground state, the wavelength of the photons (resolution in the range of 0.005 nm) being element-specific. The total number of photons is directly proportional to the concentration of the original element in the sample. Some of the photons emitted by the ICP are collected with a lens or a concave mirror. The photon beam is adjusted to a certain wavelength with a monochromator and converted into an electrical signal by a photodetector. The signal is amplified and processed by the detector electronics and then displayed and stored by a personal computer.[42] The schematic structure of an ICP-OES is shown in *figure 2.6.*

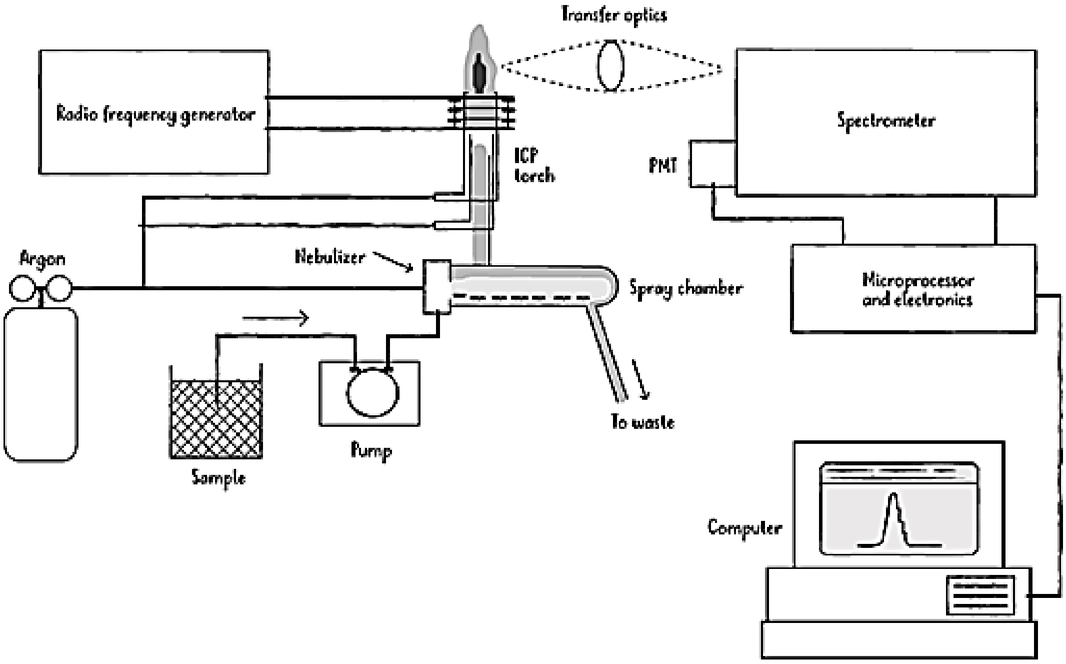


Figure 2.6: Schematic structure of an ICP-OES. [43]

2.4.4 XRF - X-ray Fluorescence Analysis

XRF is a non-destructive method for analysing the chemical element composition of a sample. It is used for the qualitative and quantitative analysis of solid and liquid materials. The concentrations of the elements are analysed regardless of their chemical bond. Practical detection limits are a few mg/kg.[44] A distinction is made between energy-dispersive and wavelength-dispersive spectrometers for X-ray fluorescence analysis, depending on the device structure and the type of fluorescence radiation detection.[45] A schematic structure of a XRF is shown in *figure 2.7*.

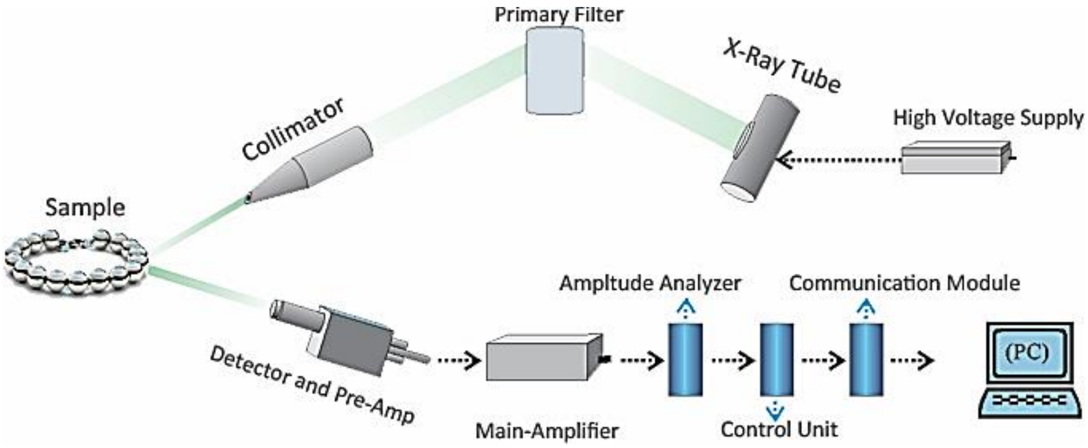


Figure 2.7 Schematic structure of a XRF.[46]

Principle:

With X-ray fluorescence analysis, the sample material to be examined is excited by a primary energy source, polychromatic X-rays from an X-ray tube, gamma or ion radiation.
Here, electrons close to the nucleus are lifted from the inner shells of the atom to those further out. This allows electrons to fall back from higher energy levels. The energy released is given off in the form of fluorescent radiation. The principle is shown in *figure 2.8*.
Each element emits a characteristic fluorescence radiation, consisting of one or more fluorescence lines of certain energy.

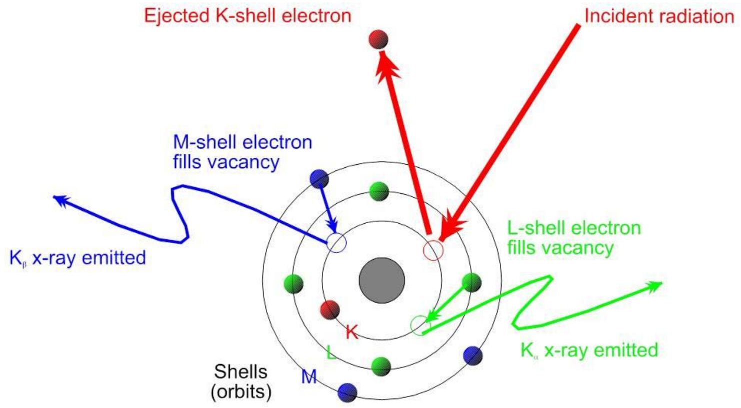


Figure 2.8: Principle of X-ray fluorescence analysis [47]

XRF always works - on metals, ceramics, soils, liquids, electrical conductors or insulators. As a method, it is independent of the sample and provides quick results. XRF can be used to analyse elements ranging from magnesium (Mg) to uranium (U). Due to physical laws, the energy and

fluorescence yield for elements with low atomic numbers decrease drastically. Therefore the "light elements" Mg, Al, Si, P and S are more difficult to measure.[48]
The challenge for a quantitative determination using XRF are matrix effects, i.e. interactions of the X-ray radiation with the sample material, such as absorption and scattering, which are strongly dependent on the sample matrix. This problem is examined in more detail in the following *section 2.4.4.1*.

2.4.4.1 Matrix effects in X-ray fluorescence analysis

The accuracy of the analysis using XRF is faced with a number of challenges due to possible matrix effects. For a better understanding of how matrix effects occur and what they depend on, the basics of XRF and the interactions that occur between the sample and X-rays are discussed first.

2.4.4.1.1 Basics of X-ray fluorescence analysis

The principle of X-ray fluorescence analysis is based on the emission of element-characteristic electromagnetic radiation, in this case X-ray fluorescence radiation, through excitation with sufficiently high energy.

When the X-ray radiation, e.g. generated in an X-ray tube, hits the sample to be analysed with sufficient energy, the electrons of the atoms are excited. The electrons from the K-, L- or M-shell can be lifted to the next electron shell. If the transmitted energy contribution of the radiation to the electron is higher than the binding energy from the electron to the nucleus, the electron can be knocked out of the atom. For example, outer electrons can be knocked out of the electron shell by completely absorbing the energy of an X-ray photon. This occurrence is called photo effect. The innermost shell (K-shell) has a higher binding energy than the next, second innermost shell (L-shell), because the bond between an electron and the atom becomes weaker, the bigger the distance from the atomic nucleus. For this reason, more energy has to be applied to excite an electron in the K-shell than for an electron in the L-shell.

By raising an electron to a higher energy level or by knocking the electron out of the atom, an unstable, excited state and at the same time an electron gap are generated. As electrons jump from the outer electron shells into the electron gap, the originally, more favourable energy state is regained. Consequently, an amount of energy equal to the difference between the energy levels involved is emitted in the form of X-ray fluorescence radiation. The energy or wavelength of the emitted radiation is characteristic of the element from which it is emitted and forms the basis for the identification of chemical elements (qualitative determination) and the determination of the concentration via the intensity (quantitative determination). The intensity is the number of X-ray fluorescence photons, measured within a certain time.

Typically, the unit cps (= counts per second) or kcps (= kilocounts per second) is given for the intensity. [45]

2.4.4.1.2 Interactions between sample and X-rays

A basic distinction of the interactions that mainly appear when the radiation enters and exits the sample is made between absorption and scattering. The strength of the interactions depends on the sample composition.

Absorption:

In this context, absorption is understood as the decrease of the incident X-rays by ionizing the outer atomic layers of the sample, which are penetrated until the detection depth is reached. Part of the characteristic radiation leaving the sample is also absorbed. Therefore, the absorption depends on the distance, which is covered, the number of atomic layers that are penetrated and the material density of the sample.[44]

Scattering:

In addition to the photo effect, scattering can also occur by a partial transfer of the energy of the incident X-ray beam to the electrons. The intensity of the scattering depends on the composition of the samples, i.e. the sample matrix. In the case of light elements, a high proportion of scattered radiation occurs, whereas elements with a heavy matrix have a relatively low scattered radiation. Furthermore, in the case of lighter elements, a second electron can be knocked out due to the energy released when the electron gap is filled (= Auger effect). A doubly ionized atom is created, which in turn leads to a reduction in the fluorescence intensity.[48] As a result, the quantitative determination of the lighter elements such as sodium and potassium is accompanied by more matrix effects and therefore it is more difficult.

In principle, a distinction is made between two types of scattering: Rayleigh scattering (also elastic or coherent scattering) and Compton scattering (also inelastic or incoherent scattering).[49] With Rayleigh scattering, the incident photons of the X-ray radiation are scattered by bound electrons. The atom is in the basic energy state. This means that the photons are scattered with unchanged energy, i.e. without releasing the energy to the electron. Rayleigh scattering mostly occurs with low energy and with elements with electrons strongly bound to the nucleus. In Compton scattering, part of the energy of the incoming photon is transferred to a loosely bound electron of an atom. How much of the energy is transferred depends on the angle of incidence of the photon. The Compton scattering mostly occurs at higher energies and thus suppresses the photo effect. [50]

2.4.4.1.3 Matrix effects

Due to the interactions of the X-ray photons with the sample material mentioned in *section 2.4.4.1.2*, the quantitative determination of the elements to be examined in the sample depends not only on the concentration but also strongly on the sample matrix. The matrix effects, based on the absorption and scattering effects mentioned above, are therefore dependent on the composition of the elements in the sample, the sample thickness, the packing density and the particle size of the sample and influence the fluorescence intensity. Attempts are made to overcome these problems by suitable sample preparation, like grinding or melting. Since in this case the samples which were used for the calibration are analysed as pressed tablets, a grinding test was carried out, as described in *section 3.2.6*, in order to determine whether matrix effects occur due to the particle size of the sample. This could be excluded for the calibration samples. [45]

A basic requirement for quantitative analysis using XRF is the production of a matrix-adapted calibration. For this purpose, sample materials with a matrix that is very similar or the same as that of the sample to be analysed must be used.

2.5 Process optimization

With a view to sustainable and environmentally friendly cement production, the process for clinker production has been continuously optimized over the past few decades. Fossil fuels were largely replaced by substitute fuels and the amount of alternative raw materials for the production of clinker was increased. Another ambition of the cement industry is the production of cements with a clinker content below 70 % through the increased use of cement additives. Reason for the increased use of additives is the high amount of CO_2 emissions, which occurs indirectly through the high energy intensity of cement production (burning process and grinding processes) and directly through the inevitable deacidification process of the calcareous raw materials.[3] Therefore the increased use of alternative input materials (substitute raw materials, substitute fuels and additives) ensured an increase in resource efficiency and recycling of waste, as well as the reduction of CO_2 emissions.

In order to still be able to achieve the highest possible quality and a wide range of possible uses, high demands are placed on both the cement product and the manufacturing process. Therefore, the following criteria must be observed when using secondary fuels and secondary raw materials [51]:

- Ecological demands
- Procedural possibilities
- Quality requirements for the product
- Employee protection concerns

The ecological demands in cement production include, above all, the reduction of emissions that have a negative impact on the environment, such as CO_2, and the entry of heavy metals. With regard to the ecological requirements, it must be taken into account that volatile organic compounds (VOC) can be released from secondary raw materials or secondary fuels. Most of the VOCs from secondary raw materials are released during the grinding process. The release of the VOCs of the secondary fuels, on the other hand, takes place when they are introduced into the secondary firing, because a dwell time of 4 seconds above 1200 °C cannot be maintained, which means that the VOCs cannot be completely destroyed. Secondary fuels with a high VOC content must therefore be used in the primary firing, where a complete destruction of the VOCs is guaranteed. Highly volatile heavy metals such as mercury (Hg) and thallium (Tl) in secondary raw materials and secondary fuels must also be taken into account.

The procedural possibilities for reducing environmental pollution include amongst others the areas of air pollution control, energy saving and water pollution control. With regard to the limits of procedural possibilities, it does not make sense, if the total energy requirement of the clinker production process increases through the use of waste. Furthermore, the use of secondary fuels in secondary firing reaches its limits where the amount of fuel used leads to excessive heating of the exhaust gas or where the material flow is hindered by the formation of deposits and crusts so that a uniform process is no longer possible. Chlorides and alkalis in particular can lead to process disruptions due to build ups and ring formation at critical concentrations, which is considered in *section 2.5.2.1* in more detail.

Other important prerequisites for an undisturbed process flow are unrestricted medium-term availability and uniform composition. Which in turn leads to the quality requirements. Some quality criteria for substitute fuels are, for example, their burning behaviour, depending on the lumpiness or grain size, or the homogeneity. The ideal burning behaviour would be immediate combustion in the combustion chamber, as is the case with thin plastic sheets. Due to 3D fractions, i.e. thicker pieces, for example shredded old tires, non-burned pieces of secondary fuels can fall into the kiln inlet and be carried along with the material flow. Because of the gas contact and the oxygen atmosphere, these pieces continue to burn. As a result, the material to be fired in the immediate vicinity enters the melting phase. The melt sticks to the powdery material or to the kiln mantle and cools down due to the significantly lower temperatures of the material or mantle compared to the gas temperatures and becomes solid. As a result, a build-up or ring can form in the kiln, which differs from the build-up and ring formations of the alkali cycles due to the formation in a closer area to the kiln inlet. Another challenge is expressed in the dosage, which must be regulated lower or higher depending on the corresponding calorific values of the substitute fuels, if the substitute fuels are inhomogeneous. Furthermore, for secondary raw materials, it must be ensured that they can be integrated into the raw mix concept and that the content of pollutants (e.g., heavy metals) in the final cement product does not grow beyond the limit values due to the use of waste. The analytical quality assurance carried out for this is examined in more detail in the experimental part (see *section 3.2*).

With regard to employee protection, radioactive and infectious waste must be excluded. [30]

The challenges in raw meal specification, procedural aspects and legal aspects, which the compliance with the above mentioned criteria entails, are described and explained in more detail in the following *sections 2.5.1, 2.5.2 and 2.6*.

2.5.1 Raw meal specifications

First of all, the optimal raw meal recipe for raw materials, substitute raw materials and corrective materials for clinker production must be determined. For this purpose, the chemical specifications lime saturation factor LSF, silica ratio SR and alumina ratio AR are used, which were explained in *section 2.1*. In order to achieve the desired chemical specifications, for example for normal meal they are LSF = 101, SR = 2.55, AR = 1.55, the control variables CaO, SiO_2, Fe_2O_3 and Al_2O_3 are adjusted by using different amounts of raw materials, substitute raw materials and correction materials. For this purpose, the control variables of the input materials must be analysed using XRF. In addition to the control variables, the secondary elements MgO, P_2O_5, SO_3, K_2O, Na_2O, TiO_2, MnO and Cl are also analysed. Depending on the properties, certain elements can have a negative impact on the cement quality if they are too high. If the phosphate content is too high, for example, there may be a disproportionate decrease in the C_3S-content in the clinker and thus have a negative effect on the strength development of the cement.[9] This is why limit values are already defined for such elements for the clinker production process.

2.5.2 Influence of the input materials on kiln operation

A change in the raw meal recipe towards an increased proportion of substitute raw materials in connection with the increasing use of substitute fuels has significant effects on the burning process of the clinker. These changes in kiln operation are discussed in more detail below.

Since the composition of the clinker results from the chemistry of the raw meal used and the ashes of the fuels used, the entire material flow input must be taken into account when assessing the burning process. In the clinker burning process, a fundamental distinction is made between the material conversion process and the incineration process. These two processes run on the counter current principle, i.e. the combustion gases and raw materials run in counter current to each other. In the drying process, the combustion gases are used not only to preheat the material flow in the preheater, but also to dry the raw materials, which leads to close contact between the exhaust gas and the raw meal. The evaporation and condensation behaviour of certain components of the raw materials and fuels creates cycles in the kiln system.[52]

These cycles are generally divided into two types, the internal and the external. The external cycle occurs between the preheater and the exhaust filter, while the internal cycle runs between the preheater and the rotary kiln. In particular the volatile elements sodium and potassium, chlorine and sulphur tend to form internal cycles.[16] In addition to the already existing base load of alkalis, sulphur and chlorides from the existing raw stone qualities from the quarry, the correction materials and fossil fuels, the increased use of substitute raw materials and substitute fuels leads to an even higher input of these elements. Due to the resulting alkali, sulphur or chloride cycles, build-ups and ring formations are possible in the rotary kiln. The total amount of alkali, sulphur and chloride compounds entered, the ratio of alkali to sulphur and chloride and the performance of the bypass system are decisive for a possible build-up or ring formation. From a chemical point of view, the most efficient lever for process stabilization is through an adaptation of the ratio of alkalis to sulphur and chloride. Therefore, in recent years, the setting of the optimal ratio, and thus the analytical recording of these elements, has become increasingly important due to the increased total load of alkalis, sulphur and chloride in combination with the plant-specific process conditions. For a better understanding of the generation of cycles and build-ups, their formation is explained below. The possibilities for reducing the number of cycles are also considered.

2.5.2.1 Formation of build-up and ring formation

In the burning process of the clinker, the alkali sulphates and alkali chlorides are formed, which are the most important cycle materials with a major influence on the kiln operation. Most of the alkalis come from the substitute raw materials used, and to a lesser, site-specific extent, from the silicate inclusions in the raw stone. Without available reactants (chloride ions, hydroxyl ions) in the gas phase, a large proportion of the alkalis remains in the clinker phase and clinker melt and only a small proportion passes into the gas phase as a volatile component.[53] This kiln condition is less critical from a process point of view, but it has an impact on the product quality, since the alkalis incorporated in the melt lead to lattice distortions of the phases formed and thus change their reaction. For example, when the alkalis are incorporated into the crystal lattice of C_3A, its symmetry changes from cubic to orthorhombic to monoclinic.[54] However, due to the combustion of high-chloride fuels or substitute fuels in the manufacturing process according to the state of the art, there are enough reactants to form volatile compounds (KCl and NaCl or KOH and NaOH) in the kiln system. The sulphur compounds carried in by the raw meal and the fuels are converted into gaseous sulphur dioxide SO_2 due to the high temperatures in the kiln.[54] If there is a sufficiently high partial pressure of SO_2 in the kiln system, the alkalis bind to alkali sulphate (K_2SO_4, Na_2SO_4) in addition to binding with chloride. [53]

This means that at a higher temperature, the vapor pressure of the compound increases at the same time, as can be seen in *figure 2.9*, which in turn means that a higher proportion of the compound is in the gas phase and thus the ion pressure in the gas phase increases. *Figure 2.9* shows the vapor pressure curves of KCl, NaCl, Na_2SO_4 and K_2SO_4 in a temperature range from 900 to 1500 °C. The vapor pressure of the alkali chlorides is shown on the primary axis, the vapor pressure of the alkali sulphates is shown on the secondary axis. In *figure 2.9* the vapor pressure is given in the outdated unit mm Hg. The conversion from mm Hg to bar is done using the factor 1.33322*10^{-3}. This means that 1 bar corresponds to approximately 750 mm Hg. A compound changes completely into the gas phase as soon as the vapor pressure of the compound corresponds to the ambient pressure. Due to the complexity of the evaporation and condensation processes in the rotary kiln, the actual ambient pressure can only be assumed. However, it is assumed that at a sintering temperature of 1450 °C and a vapor pressure of the alkali chlorides of approximately 1 bar, these alkali chlorides have completely passed from the clinker phase or melt into the gas phase. This assessment is also confirmed by the observation that only a very low chloride content of less than 0.1 wt% can be detected in the clinker. In comparison to the alkali chlorides, the alkali sulphates have a lower vapor pressure. As a result, a large part of the alkali sulphates remains bound in the clinker phase or in the melt. This integration allows the process-stable discharge via the clinker.

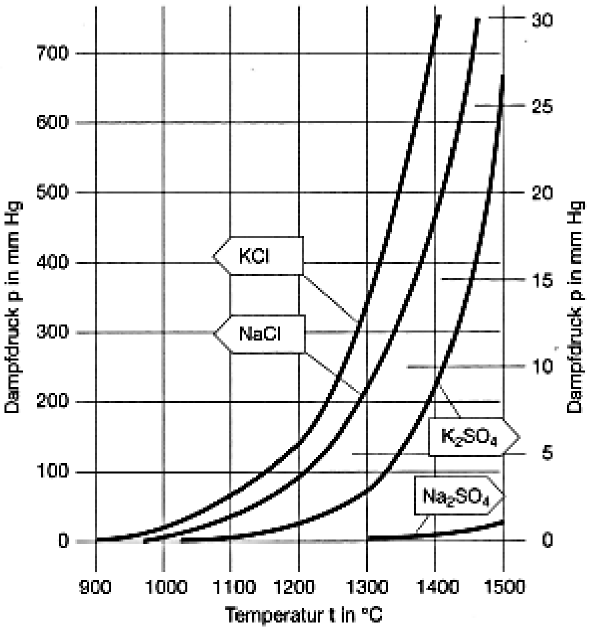


Figure 2.9: Vapor pressure of the chlorides (left y-axis) and sulphates (right y-axis) of sodium and potassium as a function of temperature. [54]

Furthermore, the temperature difference between gas flow and material flow must be taken into account. Due to the much higher gas temperatures, up to 2000 °C in the sintering zone, compared to the material temperatures, surface reactions are of great importance. The rotation of the rotary kiln at a speed of about 3 rpm allows a constant heat exchange between gas and material. For this reason, the alkali compounds already evaporate in zones in which the overall material temperature has not yet reached the critical material temperature for the evaporation of the alkalis, but where the evaporation takes place as a surface reaction due to the high gas temperatures. Thus, the volatilization of the alkalis from the clinker phases or clinker melt depends not only on a sufficient number of reactants in the gas phase but also on the size of the material surface or, from the sintering zone area, on the size of the granules formed. Analyses confirm the occurring surface reactions, since a lower concentration of alkalis was found in small granules and on the surface of larger granules.[53] This has also been confirmed experimentally at the Wietersdorf plant.

The cooling of the gas flow, the enrichment of the volatile compounds in the gas flow and the contact with the significantly colder material flow or kiln mantle contribute significantly to the condensation of the volatilized alkali compounds. The cooling of the gas flow takes place because the gas flows in the direction of the kiln inlet, i.e. into colder zones (gas temperature of the kiln inlet approx. 900 °C). Due to the accumulation of the volatile compounds in the gas phase an increased ion pressure occurs, which can lead to oversaturation and thereby the alkali compound condenses spontaneously and earlier. Upon contact with the significantly colder material flow or kiln mantle, a direct transition of the condensed alkali compounds into the solid phase can take place, since the temperature at which the alkali compounds are present in the liquid phase was skipped during the rapid cooling. The melting points of the alkali chlorides or alkali sulphates are as follows:

- NaCl: 801 °C [55]
- KCl: 770 °C [56]
- Na_2SO_4: 888 °C [57]
- K_2SO_4: 1069 °C [58]

At a low ion pressure, i.e. a low concentration of alkali compounds in the gas phase, the alkali chlorides stay longer in the gas phase and only resublimate in the preheating tower. This could lead to adhesions in the area of the oryfice, shown in green in *figure 2.10*. Alkali sulphates condense at higher temperatures than alkali chlorides and thus only contribute to a much lesser extent to the formation of adhesions in the area of the oryfice.[53] The reason for this is the lower vapor pressure of the alkali sulphates.

Some of the alkali compounds condense due to material or mantle contact before they enter the preheater, whereby a thin layer is deposited on the material or on the kiln mantle. Due to the high gas temperatures, which are in heat exchange with the surface of this material, this layer of alkali compounds remains in the melt phase and the alkali compounds can again pass into the gas phase via surface reactions. This process of evaporation and condensation inside the rotary kiln leads to the formation of alkali cycles and thus to permanent enrichment of the alkali compounds in the gas phase.

This enrichment increases the ion pressure and the condensation of the alkali compounds takes place at ever higher temperatures. If the volatile alkali compounds are oversaturated in the gas phase, spontaneous deposition can occur. The thickness of this deposited layer allows the lower part of the layer to solidify. Only the uppermost part of the layer remains liquid in direct contact with the gas phase. The spontaneously sublimated alkali compounds remain in the kiln as a build-up if they come into direct contact with the mantle. Due to the process, this form of build-up takes place within a very short time of just a few hours and has already been observed in Wietersdorf.

But even the liquid alkali compounds can lead to serious process complications after condensation. Due to the constant rotation of the rotary kiln, also the material rotates in the kiln and the liquid alkali compounds on the surface can come into contact with the powdery material or the mantle and remain stuck due to solidification. A "snowball" (formation of a sphere) or a ring formation on the kiln mantle occurs. At this point in time, a direct surface reaction with the gas phase is no longer possible and the material temperature is not yet hot enough for the alkali compounds to evaporate again. As a result of new deposits, the deposits in the kiln become larger and larger and can lead to clogging of the kiln. Then it has to be shut off and cleaned manually.

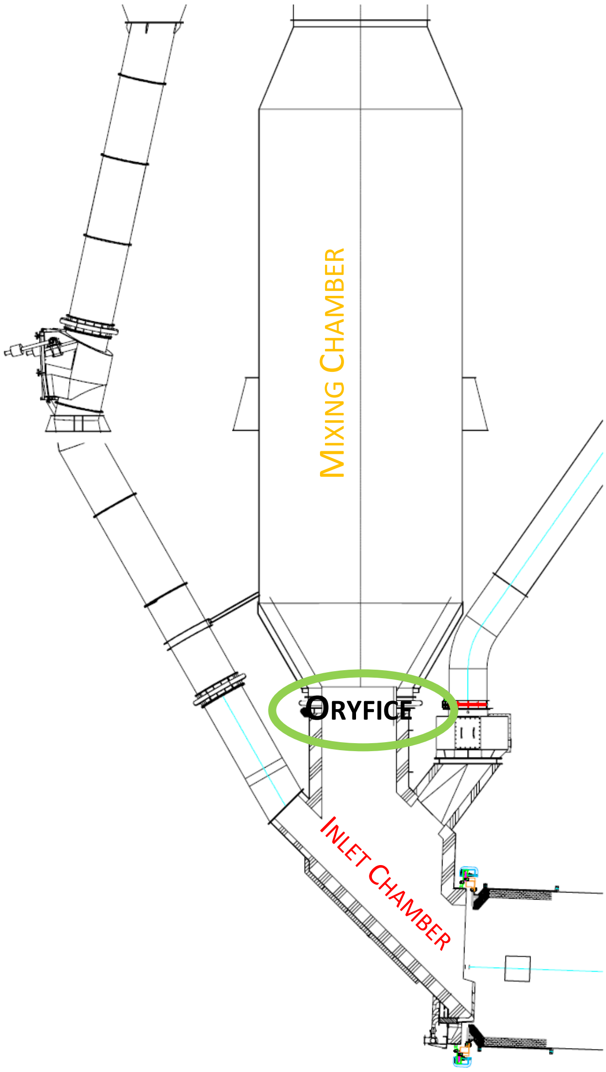


Figure 2.10: Sketch of the mixing and inlet chamber with drawn oryfice of the kiln system in the Wietersdorf plant.

2.5.2.2 Options to reduce alkali cycles

In order to prevent possible build-up or ring formation and the subsequent shut down and cleaning of the rotary kiln, intervention can be made in terms of process technology and the chemistry of the raw materials and fuels introduced. The aim in both cases is to reduce the alkali chloride load. Process-related stabilization is achieved through the operation of bypass systems. From a chemical perspective, sufficient sulphates must be made available so that the formation of the much more stable alkali sulphates is an important competitive reaction to the formation of alkali chloride. This competitive reaction is controlled via the sulphatisation degree. Furthermore, a mantle screening of the rotary kiln is carried out for the concrete assessment of these build-ups and ring formations.

2.5.2.2.1 Bypass system

Bypass systems can reduce the total load of alkalis through the targeted extraction of a portion of the air flow from the kiln inlet and, at best, prevent the enrichment of the alkaline compounds. Due to the higher vapor pressure of the alkali chlorides in conjunction with the alkali sulphates, there are predominantly alkali chlorides in the gas phase in the area of the kiln inlet and can thus be removed via the bypass flow. Decisive for the effectiveness of the bypass system is its dimensioning as well as the burner setting for temperature control of the kiln inlet. On the one hand, the bypass capacity must be designed in an appropriate ratio to the entered alkali and chloride content; on the other hand, the temperature of the gas flow in the area of the kiln inlet can be adjusted through a targeted fuel feed so that the concentration of the alkali chlorides in the gas phase can be varied. The higher the temperature, the higher the proportion of alkali chlorides and alkali sulphur compounds in the gas phase.

Theoretically, an increase in the extracted air flow could enrich the alkali and chloride content in the bypass dust and thus relieve the kiln system, but the bypass system in the Wietersdorf plant is already operating at the upper limit and has no further capacity. Another approach to preventing the formation of alkali cycles is through the targeted formation of alkali sulphates in the firing process. By increasing the amount of sulphur-containing feedstock and thus a higher availability of sulphur as a connection partner in the kiln system, the probability of the formation of alkali sulphates increases, as a result of which the remaining alkali can be discharged via the clinker. In order to determine the optimum amount of sulphur required, the sulphatisation degree is used as a control variable. This is considered in detail in *section 2.5.2.2.2.*

2.5.2.2.2 Sulphatisation degree

The sulphatisation degree or sulphate modulus is a parameter, which is used in two ways at the Wietersdorf plant. The first is to measure if there is an overall molar balance between the total inputs of sulphur and alkalis contributed by all of the raw materials, fuels and other streams entering the kiln. The second is to measure the instantaneous molar sulphur/alkali balance in the kiln, based on clinker. In both cases following equation 4.1 is used:

$$SD = \frac{\frac{SO_3}{80}}{\frac{Na_2O}{62}+\frac{K_2O}{94}-\frac{Cl}{71}} \tag{2.6}$$

In the past, there was no need to consider the chloride component due to the low chloride input from the raw materials and fuels. Therefore, the following equation 4.2 was used to calculate the sulphatisation degree:

$$SD(\%) = 77{,}4 * \frac{SO_3\,(\%)}{Na_2O\,(\%)+0{,}658\,K_2O(\%)} \tag{2.7}$$

In today's cases, however, the situation with regard to the Cl content is very different due to the high use of alternative fuels. Chloride has a very big effect on the alkali recirculation in the kiln, as it has a high affinity for binding to sodium and potassium. The volatility of alkali increases with the increase in the concentration of chloride, mainly because of the formation of more volatile alkali chlorides.[59] Generally, the output of the volatile alkali chlorides occurs via the bypass system.

The reason for considering the sulphatisation degree is that it predicts the likelihood of alkali or sulphur related build ups in different parts of the kiln system and because it affects the mineralogical composition of the clinker, if it is not in the optimal range. The sulphatisation degree of 100 means that a reaction equilibrium prevails, which reflects the optimal state. If the sulphatisation degree is below 100, there is an excess of alkalis. The sulphatisation degree above 100 means that there is an excess of sulfur. If the sulphatisation degree is too high or too low, increased volatilization occurs and can lead to ring formation. Because each plant has a plant-specific process, the resulting values of the sulphatisation degree and its effects are different from plant to plant and depend on many factors, e.g. bypass systems, variation in firing conditions, burners used, kiln temperatures, kiln dimensions, air flow, substitute fuels used, etc.

If the alkaline concentration is very high and not balanced by sulphur, the alkalis are very difficult to get out of the kiln. As a result, the alkalis will continue to recirculate within the kiln/preheat system, which in turn increases the probability of kiln rings and preheater build ups. Furthermore, some of the alkalis are incorporated into the cubic C_3A, which leads to a lattice distortion and the cubic C_3A becomes the significantly more reactive orthorhombic C_3A. If there is too much orthorhombic C_3A in the cement, problems with the processing properties of the cement like early hardening can arise due to the rapid reaction or early strength.[60] If there is an excess of sulphur in the system, the sulphur cannot bind into the clinker melt or be discharged as alkali sulphate.

However, only the sulphatisation degree is not sufficient to carry out a complete assessment of the formation of deposits and rings, since not only individual analytical parameters but the overall system must be considered. A high sulphatisation degree of the clinker can mean either that there is an excess of sulphur in the system or that a kiln coating is currently forming. While forming the kiln coating, the alkalis remain in the kiln, which gives the impression that the sulphur content is too high in the kiln. At the same time, a low sulphatisation degree does not mean that there is a too little sulphur input. It is also possibly that a too high proportion of sulphidic sulphur is introduced into the system through the raw meal. The sulphidic sulphur is emitted and is therefore lost to the analysis of the sulphatisation degree. For this reason, an additional tool, e.g. mantle screening, is required to clearly assess the sulphatisation degree in the clinker.

2.5.2.2.3 Mantle Screening

Mantle screening means that the mantle temperature of the rotary kiln is measured using a thermal imaging camera. By cooling down the mantle temperature, it can be seen that a build-up or ring formation occurs. *Figure 2.11* shows an example of the temperature recorded of the kiln at the Wietersdorf plant. In the figure, the actual state is shown as the blue curve and the historical reference state as the turquoise curve.

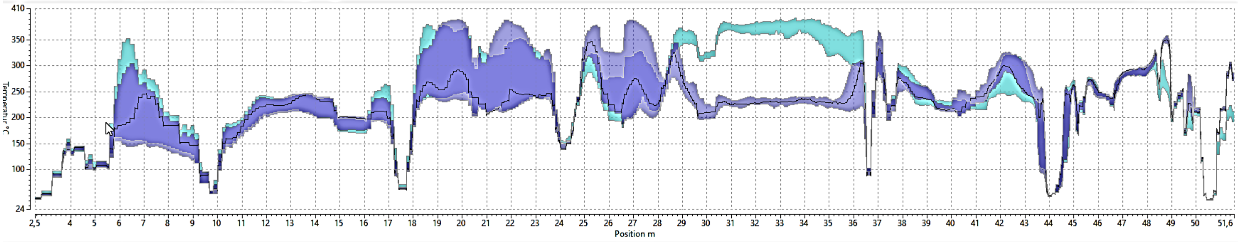


Figure 2.11: Temperature recording of a mantle screening of the rotary kiln in the Wietersdorf plant.

The kiln inlet is on the right and the burner is on the left of the *figure 2.11*. Thus, the material flow goes from right to left and consequently the gas flow from left to right, due to the counter current principle. The sintering zone is located from 0-25 m, with the upper transition zone from 18-25 m, in which a continuous coating extends because the material temperature varies due to the rotation of the kiln and thus with the alternating contact of the "cold" mantle and hot gas flow. Therefore, the material is between the still solid and transition to the liquid phase. However, this coating is to be rated positive because the kiln mantel is protected by the permanent assembly and dismantling. The preheating zone is located in the range of 25-58 m, in which no build-ups or ring formations should occur. In the range of 29-36 m, clear differences between the two temperature measurements can be seen. The turquoise curve shows kiln operation without ring formation. The blue curve, on the other hand, shows a significant drop in temperature of the mantle. The rise in the mantle temperature at 29 m means that the build-up has come loose.

In order to assess or determine the optimal kiln condition and for targeted optimization, various parameters must be considered and related. Therefore, the following factors must be taken into account:

- Entry via the raw meal (determination of the sulphatisation degree)
- Extent of the sulphidic content in the sulphur from the raw meal
- Entered chloride content via substitute fuels
- Assessment of the sulphatisation degree of the clinker, by considering the bypass dust chemistry and the sulphatisation degree of the raw meal
- Evaluation of the mantle screening
- Extent of sulphur emissions

Possible changes in the bypass dust are also decisive, since the sulphatisation degree of the clinker can be changed through higher discharge of the alkali chlorides using bypass dust. For example, by increasing the temperature of the kiln inlet or increasing the air stream drawn off, more alkalis and chlorides are discharged and therefore the sulphatisation degree of the clinker appears to be higher.

2.6 Legal aspects

From a legal point of view, the limit values for selected heavy metals in the substitute raw materials and substitute fuels used must be observed. These limit values can be found for the substitute raw materials in the document "Technical principles for the use of waste as substitute raw materials in plants for cement production" and for substitute fuels in the Waste Incineration Ordinance (WIO).

One is bound by the guideline values of the substitute fuels according to the WIO without exception, with the guideline values of the substitute raw materials according to the “Technical principles”, an additional article allows a clear extent for action. This additional article concerns compliance with the precautionary guide values for heavy metals in the product cement and the associated partial mitigation of the guide values for substitute raw materials. The product evaluation by adhering to the precautionary guide values is subject to a more holistic approach than the individual evaluation of the guide values of substitute fuels and substitute raw materials and thus all input materials, i.e. raw materials, substitute raw materials, fuels, substitute fuels and additives are considered in the precautionary guide values. For this purpose, the individual materials are analysed using XRF.

If it can be proven by a mass balance that the precautionary guideline values are adhered to in the cement produced, 10 % of the raw meal quantity may consist of substitute raw materials that exceed the guideline values of the technical fundamentals. This means that a much more variable use of substitute raw materials is possible.

In the following, the current legislation for the use of substitute raw materials and substitute fuels, the Waste Management Act (WMA 2002), the Waste Incineration Ordinance (WIO 2010) and the Technical principles for the use of waste as replacement raw materials in plants for cement production (Technical Principles) are described.

2.6.1 Waste Management Act

In addition to the general provisions, the Waste Management Act also deals with waste avoidance and recycling, general obligations and more within 10 sections.

Section 1.1 of the Waste Management Act [61] defines the goals and principles of waste management. With regard to the precautionary principle and sustainability, this must be organized in such a way that:

1. *“harmful or adverse effects on humans, animals and plants, their livelihoods and their natural environment are avoided or other effects that impair general human well-being are kept as low as possible,*
2. *the emissions of air pollutants and climate-relevant gases are kept as low as possible,*
3. *Resources (raw materials, water, energy, landscape, land, landfill volume) are conserved,*
4. *in the case of material recycling, the waste or the substances obtained from it do not have a higher hazard potential than comparable primary raw materials or products made from primary raw materials and*
5. *only waste remains, the deposit of which does not pose a risk to future generations.”* [61]

The hierarchy of the waste management objectives listed above is given in Section 1.2:

1. *“Avoidance of waste;*
2. *preparation for reuse;*
3. *recycling;*
4. *other recovery, e.g. energy recovery;*
5. *Elimination. “* [61]

The use of substitute raw materials in cement production is classified in the WMA 2002 as "material recycling". According to paragraph 2.5 in point 2:

"In the sense of this federal law," material recovery "is the ecologically appropriate treatment of waste for the use of the material properties of the starting material with the main purpose,

the waste or the substances obtained from them directly for the substitution of raw materials or of to use products made from primary raw materials, with the exception of the waste or the substances obtained from them are fed to thermal recycling. " [61]

The use of substitute fuels in cement production is classified according to WMA 2002 [61] as *"other recovery, e.g. energetic recovery".*

Further provisions on the subject of waste incineration can be found in the Waste Incineration Ordinance [62]. [38][39]

2.6.2 Waste incineration ordinance

According to paragraph 1.1 the goals of the Waste Incineration Ordinance [62] are:

1. *"the protection of life and health of people from harmful effects that can arise from the incineration or co-incineration of waste, as well as the avoidance of pollution of the environment,*
2. *the operation of incineration and co-incineration plants in such a way that emissions are kept as low as possible,*
3. *Efficiency in the application and use of energy,*
4. *in the case of co-incineration, to avoid the transfer of pollutants contained in waste, in particular heavy metals, into the product as far as possible if this poses a threat to life or health of people or a pollution of the environment."*

Because the plants for cement production are classified as co-incineration plants according to WMA 2002 [61], the second aim of the WIO is considered here in more detail. According to paragraph 7.2 of the WIO, the following requirements must be met for (co-)incineration plants:

"… Co-incineration plants must be designed, equipped and operated in such a way that the temperature of the combustion gas produced is increased in a controlled, uniform and even under the most unfavourable conditions to 850 °C for two seconds. If hazardous waste with a content of more than one percent by weight of halogenated organic substances, calculated as chlorides, is incinerated, the temperature must be increased to 1,100 °C for at least two seconds ... "[62]

Another important point that is dealt with in the WIO are the pollutants, especially those of heavy metals, and their shift from waste to the product. For this purpose, the limit values for substitute fuels when used in plants for cement production were specified in Annex 8 of the WIO [62], which means that the substitute fuels must undergo quality assurance prior to energetic recovery, which proves that the pollutant content of the substitute fuels is below the limit value.

The limit values for substitute fuels when used in plants for cement production in which cement clinker is burned are shown in *table 2.4*.

Table 2.4: Limit values for substitute fuels when used in plants for cement production.[62]

	LIMIT VALUE	
Parameter	Median [mg/MJ]	80th percentile [mg/MJ]
Sb	7	10
As	2	3
Pb	20	36
Cd	0.23 1)	0.46 1)
Cr	25	37
Co	1,5	2,7
Ni	10	18
Hg	0.075	0.15

1) For quality-assured substitute fuels (code number 91108 in accordance with the Waste Catalog Ordinance, Federal Law Gazette II No. 570/2003, in the current version), a limit value of 0.45 mg/MJ_{DM} applies for the median and a limit value of 0.7 mg/MJ_{DM}.

For the alternative fuels sewage sludge and paper fibre residues, other limit values are specified for the heavy metals Cd and Hg, which can be found in *table 2.5.*

Table 2.5: Limit values of Cd and Hg for the substitute fuels sewage sludge and paper fibre residues when used in plants for cement production.

	LIMIT VALUE	
Parameter	Median [mg/MJ]	80th percentile [mg/MJ]
Cd	0.8	0.95
Hg	0.15	0.25

Usually, the pollutant levels are expressed in two different ways:

- as absolute concentrations (mg heavy metal/kg_{DM} substitute fuel);
- as a ratio between the quantity of heavy metals and the energy content of the substitute fuel (mg heavy metal/MJ_{DM} energy content).

[63]–[65]

2.6.3 Technical principles for the use of waste as replacement raw materials in plants for cement production

The “technical principles for the use of waste as substitute raw materials in plants for cement production” are precautionary guidelines in order not to cause unnecessary environmental pollution or risks through the use of substitute raw materials in cement production.

For this purpose, principles in the area of initial inspection, organic pollutants, inorganic pollutants and external monitoring are specified, which should be taken into account during cement production.

An important point in paragraph 3 - Inorganic pollutants - are the limit values for the substitute raw materials, which must be complied with in order to be able to be used for the production of cement clinkers. The limit values are given in *table 2.6.*

Table 2.6: Substitute raw materials that are used in plants for the production of cement clinker must comply with the following limit values. [66]

PARAMETER	MEDIAN [mg/kg$_{DM}$]
Sb	30
As	30
Pb	500
Cd	5
Cr	500
Co	250
Ni	500
Hg	0.7
Tl	3

In addition, the precautionary guide values of heavy metals that should not be exceeded in the finished cement are listed. The precautionary guidelines can be found in *table 2.7.*

Table 2.7: Precautionary guide of heavy metals values in cement.[66]

PARAMETER	MEDIAN [mg/kg$_{DM}$]
Sb	15
As	15
Pb	200
Cd	4
Cr	300
Co	50
Ni	200
Hg	0.5
Tl	2

3 Experimental part

3.1 Materials

This section briefly describes the materials that are actually used in the plant Wietersdorf. The suppliers were encrypted with a code to protect the sources. The average chemistry determined for the various materials can be found in the *appendix ii*.

3.1.1 Raw materials

The basic materials for cement production are the raw stones limestone, marl and their natural mixture of grey lime, which are mined directly in the quarry next to the cement plant in Wietersdorf. The limestone quarry used in Wietersdorf is shown in *figure 3.1.* Due to the high transport costs of the raw stones limestone, marl and grey lime, which make up the majority of clinker production, it is necessary to be able to mine them in the direct vicinity of the cement works. The high transport cost intensity results from the low value of the goods and the high density. The raw stones contain the required main components CaO and SiO_2, and to a slightly smaller proportion Al_2O_3 and Fe_2O_3, as already mentioned in *section 2.2.1*.

Figure 3.1: Limestone quarry in Wietersdorf

3.1.2 Substitute raw materials

Substitute raw materials are not naturally occurring materials, but products or by-products of other manufacturing processes that, e.g. fly ash from hard coal and lignite power plants. As already mentioned in *section 2.2.2*, these can be divided into groups depending on their chemical composition. The classification is based on the chemical element, which is contained to a considerable extent and thus predominates in the composition of the raw material mixture. *Table 3.1* lists the substitute raw materials used in the plant Wietersdorf, assigned to the corresponding element group, and their origin.

Table 3.1: Substitute raw materials used in the plant Wietersdorf, assigned to the corresponding element group.

SECONDARY RAW MATERIALS	SUPPLIERS	GROUP
Boiler ash	SPLR_SRM 1	Si- Al- Fe- Ca
Filter ash	SPLR_SRM 1	
Wood ash	SPLR_SRM 2	
Wood ash	SPLR_SRM 3	
Rust ash_1	SPLR_SRM 4	
Rust ash_2	SPLR_SRM 4	
Rust ash	SPLR_SRM 2	
Rust ash	SPLR_SRM 5	
Rust ash	SPLR_SRM 6	
Fly ash	SPLR_SRM 5	
Fly ash	SPLR_SRM 7	
Fly ash	SPLR_SRM 8	
Fly ash	SPLR_SRM 6	
Drilling mud	SPLR_SRM 5	
Drilling mud	SPLR_SRM 9	
Concrete mud	SPLR_SRM 10	
C-lime dust	SPLR_SRM 11	Ca
Green liquor sludge	SPLR_SRM 12	

3.1.3 Fuels

The fossil fuels used at the Wietersdorf plant during ongoing production are exclusively hard coal. Therefore, hard coal from SPLR_F 1, SPLR_F 2 and the SPLR_F 3 are used. Natural gas is also used for starting the clinker burning process or in the case of failures.

3.1.4 Alternative fuels

Alternative fuels or secondary fuels are all types of combustible waste. These are used instead of fossil fuels. Plastics and, to a lesser extent, sewage sludge are used in the plant Wietersdorf. The substitute fuels currently used are listed in *table 3.2.*

Table 3.2: Substitute fuels used in the plant Wietersdorf with a short description of the fuel

SECONDARY FUEL	SUPPLIERS	DESCRIPTION	MATERIAL
SF A	SPLR_SF 1	High calorific fraction	Plastics
SF B	SPLR_SF 1	High calorific fraction	
SF C	SPLR_SF 2	Residues from mechanical waste processing	
SF D	SPLR_SF 3	High calorific fraction	
SF E	SPLR_SF 4	High calorific fraction	
SF F	SPLR_SF 5	Residues from mechanical waste processing	
SF G	SPLR_SF 6	Alternative fuels; quality assured	
SF H	SPLR_SF 6	Alternative fuels; quality assured	
SF I	SPLR_SF 7	Alternative fuels; quality assured; pre-shredded	
SF J	SPLR_SF 8	Alternative fuels; quality assured	
SF K	SPLR_SF 9	High calorific fraction	
SF L	SPLR_SF 9	High calorific fraction; not quality assured	
SF M	SPLR_SF 10	Alternative fuels; quality assured	
SF N	SPLR_SF 11	Residues from mechanical waste processing	
SF O	SPLR_SF 12	Sludge from biological wastewater treatment	Sewage sludge

3.1.5 Correction materials

In order to achieve the optimum raw meal composition for clinker production, correction materials have to be used in many cases, as the chemical composition cannot be achieved only with raw stone materials (limestone, marl and grey lime). The correction materials used in the Wietersdorf plant are:

- Quartzite from SPLR_CM 1
- Mill scale from SPLR_CM 2
- Mill scale from SPLR_CM 3
- Fine ore from SPLR_CM 4

3.1.6 Solidification regulator

Sulphate-containing gypsum – natural gypsum as anhydrite and REA gypsum as dihydrate – are used as solidification regulators in the Wietersdorf plant. The REA gypsum is obtained from the exhaust gases from flue gas desulphurisation systems. Therefore, the following materials are used:

- Natural gypsum SPLR_SR 1
- REA gypsum SPLR_SR 2
- REA gypsum SPLR_SR 3
- REA gypsum SPLR_SR 4

3.1.7 Additives

During cement grinding, additives used to reduce the clinker content and to reach specific properties, see *section 2.2.4*. The additives and fillers used for this at the Wietersdorf plant are as follows:

- Limestone from Wietersdorf
- Fly ash from SPLR_A 1
- Slag sand from SPLR_A 2
- Slag sand from SPLR_A 3

3.2 Quality assurance

3.2.1 Description of the analyses

For quality assurance following analysis were carry out:

3.2.1.1 Loss on ignition

1.5 g of the sample are weighed into a ceramic crucible and incinerated in a muffle furnace at 950 °C for one hour. After the sample has cooled in the exsiccator, it is weighed again and the loss on ignition can be calculated with following equation 3.1:

$$Loss\ on\ ignition\ [\%] = \frac{(mass_{input} - mass_{output}) * 100}{mass_{input}} \tag{3.1}$$

3.2.1.2 Manufacture of the fusible tablets

1 g of the sample and 5 g of lithium tetraborate are weighed into a platinum crucible and mixed. One drop of lithium bromide is added. The sample is melted for 6 minutes, after 3 minutes the liquid sample is swivelled with the tongs to remove any air bubbles. After the full 6 minutes, the liquid sample is poured into the platinum bowl and cooled with compressed air. The fusible tablets are measured using XRF.

3.2.1.3 Manufacture of pressed tablets

8 g sample and 2.5 g “Hoechst Wachs C”, which is used as a flux agent, are weighed into a can and homogenized by shaking. The homogenized sample is cold-pressed with a tablet press at 50 kN for 3 min. The pressed tablets with a diameter of 40 mm are measured using XRF.

3.2.1.4 Determination of the chloride content using a titroprocessor

For the digestion, 0.5 g of the sample is weighed onto a weighing boat. 50 ml of distilled H_2O and 15 ml of phosphoric acid H_3PO_4 1:1 (diluted) are poured into a 250 ml beaker and a stir bar is added. The solution is heated on the magnetic stirrer and the weighed sample is added. After stirring for about 2 minutes, the glass vessel is placed on the hotplate for a further

5 minutes. As the sample only partially dissolves, the solution has to be filtered off with a white band filter, which has a medium pore size of 5 µm, and rinsed with hot distilled H_2O. The beaker is cleaned with a rubber squeegee and the washing liquid is added to the filter. The filtrate is cooled to room temperature. For the titration 5 drops of concentrated HNO_3 are added to the filtrate.

Before measuring the samples, the normal factor of the $AgNO_3$ solution must be determined by analysing a reference sample (approx. 100 ml distilled water + 0.5 ml standard solution (2,336 mg/l NaCl solution) mixed with 5 drops of concentrated HNO_3) for its chloride content. Therefore, the dosing device and the Cl-electrode are immersed in the beaker and the blank sample is automatically titrated with the 0.01 N $AgNO_3$ solution at medium speed. After determining the normal factor (equation 3.2), the digested samples are titrated in the same way. In the case of samples with a low intrinsic chloride content, 0.5 ml of a standard solution is added before measurement to ensure that it is correct. After the end of the titration, the chloride content is given in [mg], which is converted into percent using the following equation 3.3 for samples without the standard solution and equation 3.4 for samples to which 0.5 ml standard solution has been added.

$$NF = \frac{V_{theoretical}}{V_{praktical}} \tag{3.2}$$

NF … normal factor

$V_{theoretical}$ … Theoretical titration volume in ml, which is required to determine the chloride content of 0.5 ml NaCl standard solution with a 0.01 N $AgNO_3$ solution (=2.00 ml $AgNO_3$)

$V_{praktical}$ … Practical titration volume in ml, which is actual required to determine the chloride content of 0.5 ml NaCl standard solution with the used 0.01 N $AgNO_3$ solution

$$Cl\,[\%] = \frac{Cl\,[mg]*100*NF}{m} \tag{3.3}$$

$$Cl\,[\%] = \frac{(Cl\,[mg]*NF)-0.7085\,mg\,Cl\,from\,NaCl\,solution*100}{m} \tag{3.4}$$

Cl … Chloride content

NF … Normal factor

m … initial weight of sample in mg

3.2.1.5 Determination of the SO_3 content using a Carbon-Sulphur-Analyser CSA

Approximately 0.15-0.25 g sample is weighed into a ceramic boat. The sample including the weight is entered in the operating software of the CSA. For the sulphur trioxide (SO_3) measurement, 0.75 g - 0.85 g Combustion Catalyst (COM-CAT) is added to the initial weight for a complete expulsion of SO_3 and mixed. After the analysis has been started with the software and the rinsing of the analyser has ended, the ceramic boat with the sample is pushed into the induction furnace. The sulphur reading is available after approximately 45-60 seconds.

3.2.1.6 Ash content

The sample, which was weighed first, is burned in a ceramic crucible overnight in a muffle furnace at 950 °C. After the sample has cooled in the exsiccator, it is weighed again and the ash content was calculated with following equation 3.5:

$$ash\ content\ [\%] = \frac{(mass_{input}[g] - mass_{output}[g]) * 100}{mass_{input}\ [g]} \tag{3.5}$$

3.2.1.7 Calorific value

To determine the calorific value, the sample is weighed and then placed with the crucible in the bomb holder. The wire and cotton thread are also attached to the bomb holder and it is ensured that the cotton thread is in contact with the sample to ensure ignition. After closing the bomb, it is filled with 30 bar oxygen and placed in the calorimeter. The sample mass and the external energies to be taken into account from the cotton thread (50 J/piece) and wire (30 J/piece) are then entered in the calorimeter. The measurement is then started and runs automatically. The resulting calorific value is displayed in J/g.

3.2.2 Procedure of quality assurance for routine samples

3.2.2.1 Raw materials and correction materials

The sampling was carried out manually from the stopped conveyor belt, as described in *section 2.3.1.* For sample preparation, the individual sample previously taken was dried overnight in a drying cabinet at 105 °C. Before and after drying, the sample was weighed to determine the moisture content of the material. When weighing the sample after drying, it was important to ensure that it had cooled down completely so as not to falsify the result. The sample was reduced to a maximum grain size of 15 mm using a jaw crusher. Subsequently, the amount was reduced to one third with a riffle splitter. This third was ground with a vibrating disc mill for a certain time, which varies depending on the material of the sample. The duration of the grinding can be found in *table 3.3*. The finely ground sample was filled into a suitable container, carefully sealed and labelled with the date and material. The quantities required for the analyses were taken from this container and the remaining sample material was kept as a reserve sample.

Table 3.3: Milling times of the different materials.

MATERIAL OF SAMPLE	TIME [s]
LIMESTONE	30
MARL	30
GREY LIME	30
QUARTZITE	30
FINE ORE	30
MILL SCALE	60
FLY ASH	30
SLAG SAND 1	30
SLAG SAND 2	20
GYPSUM NATURE	15
GYPSUM REA	5
RUST ASH_1	10
RUST ASH_2	25
RUST ASH_3	10
BOILER ASH	25

Analysis for raw materials: The raw materials were analysed for their chemical composition (main elements as oxides), including SO_3 and chlorides, and for their heavy metal content using an X-ray fluorescence analyser. A pressed tablet had to be produced for the XRF analysis.

Analysis for correction materials quartzite and fine ore: For quartzite and fine ore, an analysis of the chemical composition was carried out using XRF. Therefore, a fusible tablet was produced out of the residue of the loss on ignition, which was determined before. For the analysis of the heavy metal content, a pressed tablet was produced and a XRF analysis was carried out. The SO_3 content was determined with the carbon-sulphur analyser. In addition, the chloride content was determined wet-chemically using a titroprocessor.

Analysis for correction material mill scale: For the correction material mill scale, an analysis of the chemical composition and heavy metal content was carried out. For that, only a pressed tablet had to be produced, since mill scale has a higher content than 0.5 % of total organic carbon (TOC), the platinum crucible would be damaged during the manufacture of the fusible tablet. Also, the chloride content was determined wet-chemically using a titroprocessor.

The procedure of loss on ignition, the production of melt and pressed tablets, and the determination of the chloride and sulphur content are briefly described below.

3.2.2.2 Substitute raw materials

The individual samples of the substitute raw materials were provided in a well-sealed and carefully labelled 0.5 kg plastic can. The sample preparation was carried out in the same way as described for the raw materials and correction materials in *section 3.2.2.1.*

From the substitute raw materials, the loss on ignition, the chemical composition using the fusible tablet, the heavy metal content using the pressed tablet, the chloride content and SO_3 content were determined. The procedure was identical to the procedure of the correction materials quartzite and fine ore, which was described in *section 3.2.2.1.*

3.2.2.3 Substitute fuels

Plastics: Spot samples are drawn from every plastic delivery (<50 mm), separated by origin and grain size. These spot samples are combined into daily samples, reduced to approximately 500 g by “dividing into four”, dried at 105 °C and the humidity determined. – “Dividing into four“ means that the sample is divided into four equal parts and then two diagonally opposite parts are discarded. The remaining parts are then homogenized. The process is repeated until the desired amount is reached. – The sample is then reduced to <1 mm using a cutting mill, is filled into 0.5 kg plastic cans and placed in a collection box and is brought daily to the laboratory. The substitute fuel samples, shredded to <1 mm, are processed further in the laboratory as follows:

To reduce the sample amount, “dividing into four” was used again. The process is repeated until 2 quarters of the material result in a total of 20 g, whereby it is essential that the fines must be retained in the sample during the quartering. The 20 g sample are then comminuted to <0.5 mm using a centrifugal mill. The ground sample is then placed in the corrugated divider and divided once. This results in approximately 10 g each in both bowls. The contents of one bowl are now processed into a melt-pressed tablet for heavy metal analysis using XRF. The melt-pressed tablet with a diameter of 40 mm was hot-pressed at 30 kN for 7 min with heat (180 °C) and for 4 min with cooling. The contents of the other bowl are now divided again. This process is repeated 3 times. Thus, approximately 8.75 g of sample are obtained in one bowl and 1.25 g in the other bowl. The contents of the first bowl (8.75 g) are used as a reserve sample. The contents of the second bowl (1.25 g) are divided again and processed into two small hand pressed pellets, which are used for the determination of the ash content and calorific value. For the analysis of the plastics, their ash content, calorific value, chlorine and heavy metal content are determined.

Sewage sludge: Sampling and sample preparation are identical to those for the plastic samples, except that the sewage sludge is not ground with the centrifugal mill, but with the vibrating disc mill for 30 s. The pressed tablet is manufactured as described in *section 3.2.1.3*. For the analysis of the sewage sludge, its ash content, calorific value, chlorine and heavy metal content are determined.

3.2.3 Procedure of quality assurance for process samples

The sampling of the process samples is carried out either automatically using collective samples or manually using random samples. The collective samples are continuously and automatically taken from the running conveyor belt with an airslide sampler or a screw sampler and collected over a defined sampling period. The manual sample is carried out as described in *section 2.3.1.* The following *table 3.4* summarizes the sample type, sample period, number of samples and analyses of the various process samples.

Table 3.4: Sample type, sample period, number of samples and analyses of the process samples.

PROCESS SAMPLE	SAMPLE TYPE	SAMPLE PERIOD	NUMBER OF SAMPLES	ANALYSIS
RAW MEAL	COLLECTIVE SAMPLE	30 min	2/h	XRF; SIEVE RESIDUE
KILN INLET	COLLECTIVE SAMPLE	20 min	1/h	XRF
BYPASS DUST	SPOT SAMPLE	-	6/d	XRF; XRD
HOT MEAL	COLLECTIVE SAMPLE	120 min	12/d	XRF
CLINKER	SPOT SAMPLE	-	1-2/h (DEPENDS ON THE QUALITY)	XRF; XRD; COLOUR ANALYSIS; FREE TIME (WET CHEMICAL); FE(II)
CEMENT	COLLECTIVE SAMPLE	15 min	1/h	XRF; XRD; COLOUR ANALYSIS; FINENESS OF GRAIN

The samples taken are sent to the POLAB using a pneumatic transportation system, where they are processed directly into pressed tablets by a robot if necessary for analysis. These pressed tablets are automatically transported to the analysers and analysed by XRF, XRD and colour analysis. As part of this work, the XRF-data, the chemical composition including SO_3 and chloride content as well as the heavy metal content, were collected.

3.2.4 Procedure of quality assurance for additives and solidification regulators

The sampling was carried out manually from the stopped conveyor belt, as described in *section 2.3.1.* The sample preparation of the solidification regulators and additives were carried out according to the same principle as for the raw materials and correction materials, which were described in *section 3.2.2.1.*

The heavy metal content using pressed tablets and the chloride content of the solidification regulators and additives were determined. The procedure was identical as for the correction materials quartzite and fine ore, which was described in *section 3.2.2.1.*

3.2.5 Procedure of quality assurance for alkali, sulphur and chloride calibration samples

The sampling of the spot samples for the alkali calibration was carried out manually from the stopped conveyor belt as described in *section 2.3.1*, but a larger amount was taken. The sample preparation for limestone, marl and clinker was carried out in accordance with *section 3.2.2*. The kiln inlet, hot meal and bypass dust are already suitable for analysis after the sampling and no longer had to be prepared.

In order to know the exact initial concentration of Na_2O and K_2O of the reference values, a sample of each reference for the alkali calibration was sent to the Wessling GmbH reference laboratory and measured using ICP-OES. The SO_3 and chloride content was analysed as described in *section 3.2.1*. To establish the calibration, the reference and 4 mixed samples (reference + certain amount of KCl and Na_2SO_4) were manufactured for each substance. For the manufacturing of the mixed samples, previously calculated weights of KCl and Na_2SO_4 were added and homogenized for 20 min using a turbo mixer. The weights of the chemicals added and the calculated chemical concentration of K_2O, Cl, Na_2O and SO_3 are listed in *table 3.5.* The equations used and the calculation steps for the calculation of the chemical concentrations for the mixed samples can be seen in the *appendix iii.*

Basically, a given concentration of the standards, which are used, is required for a calibration line for the XRF. These standards are then measured using XRF. To create the calibration line, the measured intensity is plotted against the given concentration of the standards. For the alkaline calibration, a pressed tablet was made from all reference and mixed samples. The calculated values of the reference and mixed samples (K_2O, Na_2O, SO_3 und Cl), which are given in *table 3.5*, were stored as a standard and thus formed the theoretical value. The pressed tablets analysed with the XRF were measured to the respective theoretical values and the measured and corrected count rate [kcps] was plotted against the theoretical chemical concentration [%].

Table 3.5 shows the weight, weights of the chemicals added and the calculated chemical concentration of K_2O, Cl, Na_2O and SO_3 for the blind and mixed samples of each process sample.

SAMPLE	WEIGHT [g]	KCL_ADD [g]	K_2O [%]	CL [%]	NA_2SO_4_ADD [g]	NA_2O [%]	SO_3 [%]
BYPASS DUST							
BPS_16.00 BP	300.00	0.00	11.90	8.54	0.00	1.30	3.56
BPS_16.00 P1	320.23	13.01	13.71	9.93	7.22	2.20	4.61
BPS_16.00 P2	336.60	22.51	14.83	10.79	14.09	2.99	5.53
BPS_16.00 P3	360.10	39.13	16.78	12.28	20.97	3.62	6.25
BPS_16.00 P4	381.34	56.93	18.79	13.82	24.41	3.82	6.41
KILN INLET							
OE BP	500.00	0.00	0.75	0.07	0.00	0.18	0.55
OE P1	501.78	0.40	0.80	0.10	1.38	0.30	0.70
OE P2	504.46	0.79	0.84	0.14	3.67	0.50	0.96
OE P3	507.15	1.19	0.89	0.18	5.96	0.69	1.20
HOT MEAL							
HM BP	500.00	0.00	4.00	2.16	0.00	0.50	2.03
HM P1	509.00	4.56	4.50	2.55	4.44	0.87	2.49
HM P2	522.65	12.48	5.34	3.20	10.17	1.33	3.04
HM P3	536.29	20.39	6.13	3.82	15.90	1.76	3.57
HM P4	557.63	30.28	7.02	4.52	27.35	2.59	4.59
CLINKER							
KLI BP	500.00	0.00	0.83	0.04	0.00	0.38	0.61
KLI P1	502.34	1.31	0.99	0.16	1.03	0.47	0.72
KLI P2	505.83	2.50	1.13	0.27	3.33	0.66	0.97
KLI P3	509.30	3.68	1.27	0.38	5.62	0.85	1.22
KLI P4	513.18	5.27	1.46	0.53	7.91	1.04	1.46
LIMESTONE							
KS BP	500.00	0.00	0.05	0.00	0.00	0.01	0.05
KS P1	500.85	0.32	0.09	0.03	0.53	0.06	0.11
KS P2	501.81	0.71	0.14	0.07	1.10	0.11	0.17
KS P3	505.56	3.88	0.53	0.37	1.68	0.15	0.24
KS P4	512.64	9.82	1.26	0.91	2.82	0.25	0.36
MARL							
ME BP	500,00	0,00	1,20	0,00	0,00	0,32	0,76
ME P1	500,72	0,14	1,22	0,02	0,58	0,37	0,82
ME P2	501,68	0,53	1,26	0,05	1,15	0,42	0,89
ME P3	503,04	1,32	1,36	0,13	1,72	0,47	0,95
ME P4	507,57	5,28	1,84	0,50	2,29	0,51	1,00

3.2.6 Procedure of quality assurance for grinding test samples

In order to exclude matrix effects from the sample preparation of the reference and mixed samples for the alkalis (K and Na), a grinding test with different grinding times and chemicals was carried out on the process and raw stone samples. The samples for the grinding test were made from the prepared reserve samples from the alkali calibration.

For bypass dust, only chemicals with potassium (KCl, $KHSO_4$ and K_2SO_4) were added to the mixed samples, since the calibration for sodium was already suitable. For limestone, marl and kiln inlet, mixed samples for potassium and sodium were produced by using 4 different mixtures of chemicals (KCl/Na_2SO_4; KCl/NaCl; K_2SO_4/Na_2SO_4; K_2SO_4/NaCl). For the hot meal and clinker grinding test, 2 mixtures (Na_2SO_4/K_2SO_4; K_2SO_4/NaCl) were produced. The exact weights of the chemicals are given in *table 3.6* below.

Table 3.6 shows the weight, weights of the chemicals added for the grinding test samples.

BYPASS DUST

SAMPLE	KCL [g]	NA_2SO_4 [g]	K_2SO_4 [g]	NACL [g]	$KHSO_4$ [g]	WEIGHT [g]
BPS P1	10.02	-	-	-	-	310.02
BPS P2	10.02	-	-	-	-	310.02
BPS P3	-	-	-	-	18.30	318.30
BPS P4	-	-	23.42	-	-	323.42
BPS P5	-	-	23.42	-	-	323.42
LIMESTONE						
KS P1	1.13	0.31	-	-	-	151.44
KS P2	1.13	-	-	0.13	-	151.26
KS P3	-	0.31	2.64	-	-	152.95
KS P4	-	-	2.64	0.13	-	152.77
MARL						
ME P1	0.95	0.62	-	-	-	151.57
ME P2	0.95	-	-	0.25	-	151.20
ME P3	-	0.62	2.22	-	-	152.84
ME P4	-	-	2.22	0.26	-	152.48
KILN INLET						
OE P1	0.30	1.10	-	-	-	151.4
OE P2	0.30	-	-	0.45	-	150.75
OE P3	-	1.10	0.69	-	-	151.79
OE P4	-	-	0.69	0.45	-	151.14
HOT MEAL						
HM P1	-	0.86	2.78	-	-	153.64
HM P2	-	-	2.78	0.35	-	153.13
CLINKER						
KLI P1	-	0.41	1.86	-	-	152.27
KLI P2	-	-	1.86	0.17	-	152.03

The K_2O and Na_2O values calculated from the exact weights for the individual mixed samples and for the reference samples are given in *table 3.7* below.

Table 3.7 shows the chemicals added and the calculated chemical concentration of K_2O and Na_2O for the grinding test samples.

BYPASS DUST

SAMPLE	CHEMICALS_ADDED	K_2O [%]	Na_2O [%]
BPS BP	-	15.78	-
BPS P1	KCl	17.31	-
BPS P2	KCl_GROUND	17.31	-
BPS P3	$KHSO_4$	16.86	-
BPS P4	K_2SO_4_GROUND	20.76	-
BPS P5	K_2SO_4	20.76	-
LIMESTONE			
KS BP	-	0.75	0.18
KS P1	KCl/Na_2SO_4	0.52	0.10
KS P2	KCl/$NaCl$	0.52	0.06
KS P3	K_2SO_4/Na_2SO_4	0.98	0.10
KS P4	K_2SO_4/$NaCl$	0.98	0.06
MARL			
ME BP	-	1.20	0.32
ME P1	KCl/Na_2SO_4	2.00	0.50
ME P2	KCl/$NaCl$	2.00	0.41
ME P3	K_2SO_4/Na_2SO_4	1.97	0.50
ME P4	K_2SO_4/$NaCl$	1.97	0.41
KILN INLET			
OE BP	-	0.75	0.18
OE P1	KCl/Na_2SO_4	0.28	0.50
OE P2	KCl/$NaCl$	0.28	0.50
OE P3	K_2SO_4/Na_2SO_4	1.00	0.50
OE P4	K_2SO_4/$NaCl$	1.00	0.50
HOT MEAL			
HM BP	-	4.00	0.50
HM P1	K_2SO_4/Na_2SO_4	4.91	0.75
HM P2	K_2SO_4/$NaCl$	4.91	0.62
CLINKER			
KLI BP	-	0.83	0.38
KLI P1	K_2SO_4/Na_2SO_4	1.48	0.50
KLI P2	K_2SO_4/$NaCl$	1.48	0.44

The grinding times used for the various samples are shown in *table 3.8.* In order to be able to recognize possible matrix effects, at least twice the grinding time was used as in normal operation.

Table 3.8: Used grinding times depending on the process samples.

SAMPLE	GRINDING TIME_1 [s]	GRINDING TIME_2 [s]	GRINDING TIME_3 [s]
BYPASS DUST	45	70	95
LIMESTONE	30	90	-
MARL	30	90	-
KILN INLET	30	90	-
HOT MEAL	45	100	-
CLINKER	60	120	-

After the grinding process, one pressed tablet was produced for each sample and grinding time, which were then measured using XRF. The resulting values are given in *table 4.6* and *table 4.7* in *section 4.3* and compared with the calculated values.

3.3 Analysis Methods

The analysis equipment and measurement methods used are briefly described in the following section.

3.3.1 RFA

The X-ray fluorescence analyser used was the Axios max or Zetium from PANalytical which are equipped with a wavelength-dispersive mode of operation. The spectrometer settings used can be seen in *table 3.9.* The Axios max uses PANalytical's SuperQ software. By creating different calibrations, a large number of different samples can be analysed.

The calibration Omnian was used to analyse the chemical composition. Omnian is a standards-free analytical method that can be used when an associated method or certified standards are not available for the sample. Thus, samples can be analysed regardless of the sample type or matrix.[67]

The calibration Pro-Trace was used for the heavy metal analysis. Pro-Trace is a reliable trace element analysis, which is for the calculation of the net intensities and the exact matrix correction if the total matrix is unknown.[68]

Table 3.9: Spectrometer setting of the Axios max and Zetium X-ray fluorescence analyser.

ACTUAL STATE		
Setting parameter	Axios max	Zetium
Conductivity [µS/m]	23.93	25.40
Internal Flow [l/min]	3.790	3.730
External Flow [l/min]	4.170	4.180
Cabinet Temperature [°C]	30.00	30.01
Primary Temperature [°C]	17.10	15.20
Vacuum Level [Pa]	1.45	2.39
Medium	Vacuum	Vacuum
X-RAY GENERATION		
Setting parameter	Axios max	Zetium
Voltage [kV]	32	25
Current [mA]	75	160
OPTICAL PATH		
SETTING PARAMETER	AXIOS MAX	ZETIUM
Beam Filter	Brass (400 µm)	Brass (400 µm)
Mask Diameter	37	35
Collimator [µm]	150	300
Crystal	LIF 200	GE 111-C
Angle [°]	113.1150	110.7126
DETECTOR SETTINGS		
Setting parameter	Axios max	Zetium
Gas Flow [l/h]	1.0	1.0
Gas Pressure [hPa]	810.7	968.0

3.3.2 ICP-OES

The ICP-OES reference measurements for XRF were carried out in an external company (Wessling GmbH; Germany). The Varian Vista AX CCD Simultaneous ICP-AES was used as the analysis device. The set measurement parameters are listed in *table 3.10.*

Table 3.10: Set measurement parameters of the Varian Vista AX CCD Simultaneous ICP-OES.

PARAMETER	MEASUREMENT SETTING
Method	Minst
Gas flow [l/min]	16.5
Auxiliary gas [l/min]	1.5
RF power [kW]	1.2
Nebulizer uptake rate [kBa]	200
Plasma	Axial
Integration time [s]	20
Wavelength [nm]	766.491 (K); 568.821 and 588.995 (Na)

3.3.3 CSA

The SC-144DR Dual Range Carbon-Sulphur Analyzer was used. The SC-144DR is equipped with a resistance furnace and an infrared detection system. To guarantee complete combustion of the sample, the temperature in the incinerator is 1382 °C. The minimum and maximum integration times for low and high sulphur content and for carbon are given in *table 3.11.*

Table 3.11: Minimum and maximum integration times for low and high sulphur content and for carbon of the CSA.

	LOW S CONTENT	HIGH S CONTENT	CARBON
MINIMUM INTEGRATION TIME [s]	120	60	40
MAXIMUM INTEGRATION TIME [s]	240	180	180

The measurement was carried out using method C 12-48. Before measuring, the method had to be calibrated with sulphur and carbon. For the calibration of sulphur, the coal standard PART NO. 502-671 by LECO with a heavy sulphur content of 1.14 ± 0.03% was used. Calcium carbonate LCRM® with a carbon content of 11.99 ± 0.05% was used as a certified reference material for the calibration of carbon.

3.3.4 Calorimeter

The calorimeter IKA® C 7000 with a double-dry measuring method and isochoric sample digestion, the IKA® C 7002 cooling system and the cooling water supply KV400 from IKA were used to measure the calorific value. When determining the calorific value, the maximum energy input into the decomposition vessel of 40,000 J, an operating pressure of 230 bar and the maximum permissible operating temperature of 50 °C must not be exceeded. The appropriate amount of sample must be used for this. The measurement results are given as the calorific value in [J/g].

3.4 Evaluation methods

3.4.1 Excel

Excel, a spreadsheet program, was used for the evaluations and calculations of the calibrations and mass balances. The Excel Solver, an Excel add-in program, was also used to calculate the mass balances. The solver is a tool for solving multidimensional systems of equations. The solver can be used to determine the optimal value for an equation by specifying secondary conditions or restrictions on the output values. To calculate the formulas, selected input values are viewed as variable and can be changed to find the optimal solution to the equation. Thus, the solver adjusts the variable values so that they meet the secondary conditions and achieve the desired result. The exact calculation steps are attached to the *appendix iv*.

3.4.2 LIMS – Laboratory Information Management System

LIMS was mainly used for the administration of the samples and measurement data. Therefore, all information (date of receipt, storage, origin, analysis date, etc.) of the samples were stored in the system. The automatic data integration of analysis devices (e.g. XRF) ensures secure data management, timesaving data processing and secure access to data from various devices.[69] The program XRMiniLIMS was used for this.

3.4.3 Assessment

The mean value and the standard deviation were calculated to assess the measurement results. To determine the mean value, the arithmetic mean was calculated using the following equation 3.6:

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \tag{3.6}$$

The standard deviation σ, which is determined using the following equation 3.7, serves as a measure of the spread of the measured values around the mean value:

$$\sigma_x = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n} (x_i - \bar{x})^2} \tag{3.7}$$

σ_x is a positive quantity which becomes zero if all measured values agree.[70]

To assess the XRF calibration line, the assessment criteria slope (E), intercept (D), root mean square error (RMS) and the correlation were used. The slope E shows the sensitivity of the measurement and is calculated using the following equation 3.8 [71]:

$$E = \frac{\sum_{i=1}^{n}[(x_i-\bar{x})\cdot(y_i-\bar{y})]}{\sum_{i=1}^{n}(x_i-\bar{x})} \tag{3.8}$$

The intercept D specifies the value where the calibration line intersects the zero point on the x-axis. When using background-corrected intensities, measured intensity versus calculated intensity should go through 0. The intercept is calculated using the following equation 3.9:

$$D = \bar{y} - E\bar{x} \tag{3.9}$$

The root mean square error is the standard deviation of residuals. Residuals indicate the distance between the measured data points and the calibration line. The RMS is therefore a way of determining the accuracy of the calibration line and is calculated using the following equation 3.10:

$$RMS = \sqrt{\frac{\sum_{i=1}^{n} \left(y_i - \hat{y}_i\right)^2}{n}} \qquad (3.10)$$

The correlation indicates the relationship between the measured and calculated values of the standards and should be close to 1.

4 Evaluation

In order to achieve a target-oriented handling of the above-mentioned challenges (*section 2.5* and *2.6)* and a simpler assessment of the process and the input materials as well as the product cement, a mass balance was developed as part of this master's thesis.

4.1 Development of the material balance

In this way, for example, process-relevant problems, as described in *section 2.5.2*, can be identified and remedied in advance, or compliance with legal aspects, such as the specified precautionary guidelines for heavy metals in cement, can be guaranteed.

Basically, two different system boundaries were defined for the development of the mass balance. For the process-related effects, only the clinker burning process has to be taken into account. The system limits for process optimization, as shown in *figure 4.1*, were thus established.

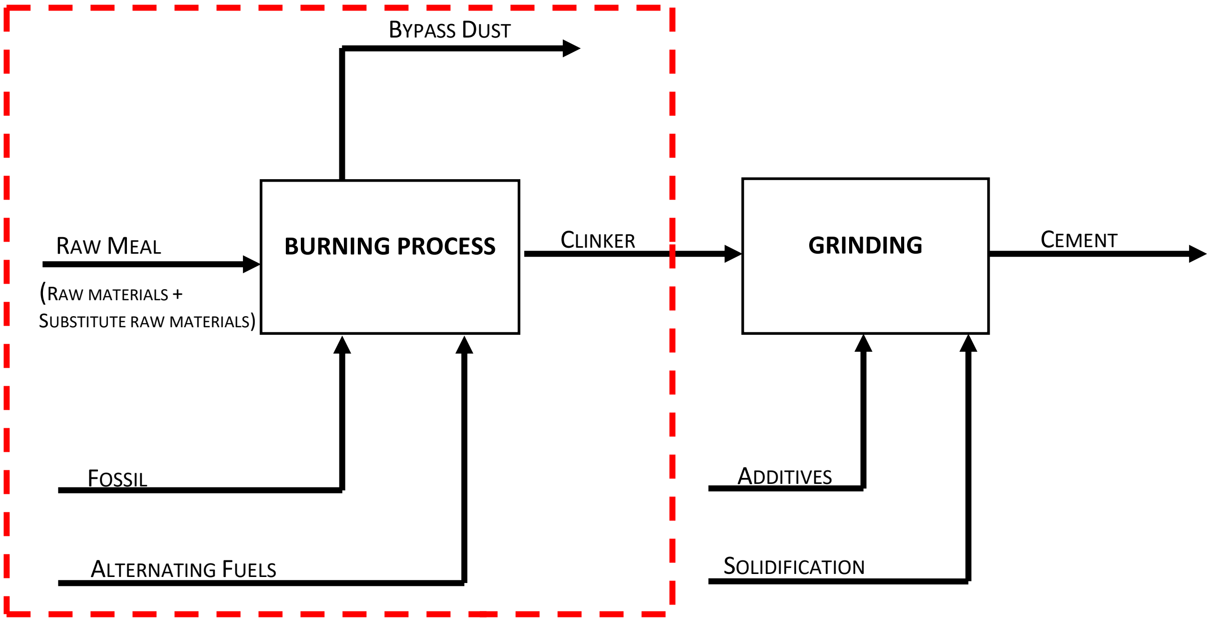


Figure 4.1: System boundaries (red dashed line) of the material balance for process optimization.

For the compliance with the heavy metal limit values in cement production, as explained in *section 2.6,* the system boundaries have been expanded. Therefore, in addition to the clinker production process, cement grinding is also taken into account, as shown schematically in *figure 4.2*.

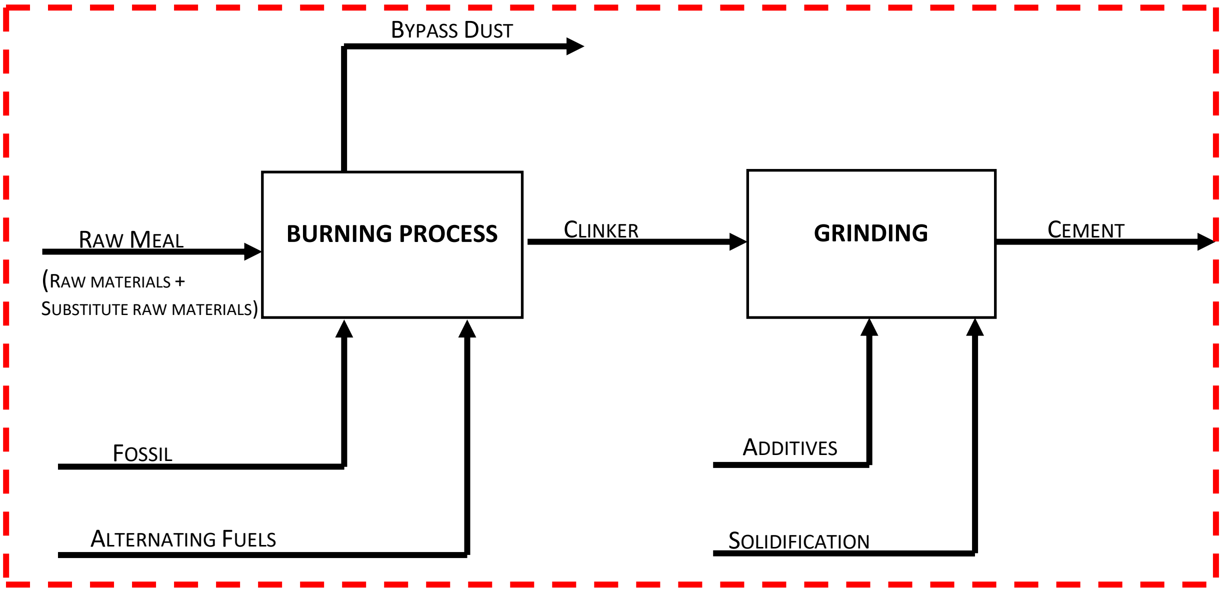


Figure 4.2: System boundaries (red dashed line) of the material balance for compliance with the heavy metal limit values.

The data required for this mass balance were analysed as discussed in *section 3.2* and evaluated using Excel and Lims, which was described in *section 3.4.* For a better understanding of the individual material flows, these are described in more detail below.

Fossil fuels: The 'Fossil Fuels' material flow consists of the coal used, which is supplied by different companies. Coal is one of the conventional energy sources and is mainly used because of the constant calorific value and thus the stabilization of the temperature in the kiln.

Substitute fuels: The 'Substitute Fuels' material flow is made up of various substitute fuels. In the example of the company "w&p Zement GmbH", these consist predominantly of various plastics, which make up about 71 % of the total amount of fuel. Sewage sludge is also used as a further substitute fuel, which makes up 16 % of the fuel quantity. *Table 4.1* shows the percentage distribution of the fuels used and their input.

Table 4.1: Input per hour and percentage distribution of the fuels used.

FUEL	INPUT [t/h]	MASS DISTRIBUTION [%]
FOSSIL FUELS	2.08	13
PLASTICS	10.98	71
SEWAGE SLUDGE	2.44	16

Raw meal: The material flow 'Raw Meal' consists of the raw materials and the substitute raw materials. In this case, the constituents of the raw material are limestone, marl and grey lime, which are transported directly from the quarry to the cement works. In addition to mill scale, fine ore, quartzite, slag and plaster, the substitute raw materials also contain various ashes, such as fly ash, soda or boiler ash, or sludge. The individual substances have already been dealt with in more detail in the experimental part in *section 3.1.* The use of the various substances depends on their chemical composition and whether they are available in sufficient quantities.

Bypass dust (BPS): The material flow 'Bypass Dust' is drawn off directly after the kiln or at the kiln inlet in order to prevent the internal alkali or chloride circuits and thus to ensure an undisturbed course of clinker production. The amount of bypass dust, and thus of volatile substances, that is removed can be adjusted by the bypass dust rate after use. Usually, the bypass dust rate is about 1 %.

Clinker: The 'Clinker' material flow is determined via the amount of raw meal and fuel used via the loss on ignition or ash content. During the burning process, CO_2 is emitted, which in turn is associated with a loss of mass of the starting materials. In addition, the 'bypass dust' material flow must be removed in order to obtain the final clinker material flow.

Additives: At the Wietersdorf plant, the material flow 'Additive' consists of different compositions of slag, fly ash and limestone. The proportion of additives depends on the type of cement produced and can make up to 20 % of the cement content. The properties of the additives affect the resulting cement.

Solidification regulator: For the 'Solidification Regulator' mass flow sulphate carriers are generally used. Natural gypsum and REA gypsum (anhydride and dihydrate) are used for this at the Wietersdorf plant.

4.1.1 Theoretical calculation of the system using LSF, SR and AR

As explained in *section 3.2*, the chemical composition and heavy metals of the individual substances were measured using XRF. In addition, the loss on ignitions were analysed gravimetrically and the chloride content was analysed using a wet chemical method. The SO_3 values were determined using CSA.

An average chemistry of the individual substances was calculated from the evaluated data. In order to be able to evaluate and characterize the raw meal properties and clinker properties more easily, the lime saturation factor LSF, the silica ratio SR and the alumina ratio AR were calculated. The Excel solver was used to calculate a recipe according to defined specifications for the raw meal chemistry and the defined amount of certain substitute raw materials used. The user can select the substitute raw materials that should be used and specify their desired percentage. The other raw materials are calculated via the solver in such a way that the constraints of the solver, which are listed below, are fulfilled.

Constraints:

- The lime saturation factor LSF is in the range from 101 to 103
- The silica ratio SR is in the range from 2.45 to 2.6
- The alumina ratio AR is in the range from 1.5 to 1.6

- The recipe must reach 100%
- The use of mill scale is below 0.4%
- The use of grey lime is 25%

LSF, SR and AR are used to determine the main element content. Mill scale must be limited because of the input of chrome, which forms [Cr(VI)] during the burning process, since the upper limit in the cement must be complied. Otherwise, the chromate has to be reduced with a reducing agent, which is associated with a high-cost factor. The definition of the grey lime content is conditioned by the quarry specifics.

The fuel chemistry was also calculated using the percentage of used fuels and alternative fuels. In order to maintain the clinker + bypass dust chemistry, the used raw meal recipe and fuel recipe must be weighted with the ignition losses or ash content, respectively, and then normalized again to 100 %. Due to the CO_2 emission and the associated loss of mass during the firing process in the rotary kiln, a higher percentage of the individual components of the chemical composition of the raw meal remains, which is why the oxides must be converted without the loss on ignition. For this, the following formula is used, shown using the example of Na_2O:

$$Na_2O_{loss\ on\ ignition\ free}\ [\%] = Na_2O\ [\%] + (Na_2O\ [\%]\ * loss\ on\ ignition\ [\%]/100) \quad (4.1)$$

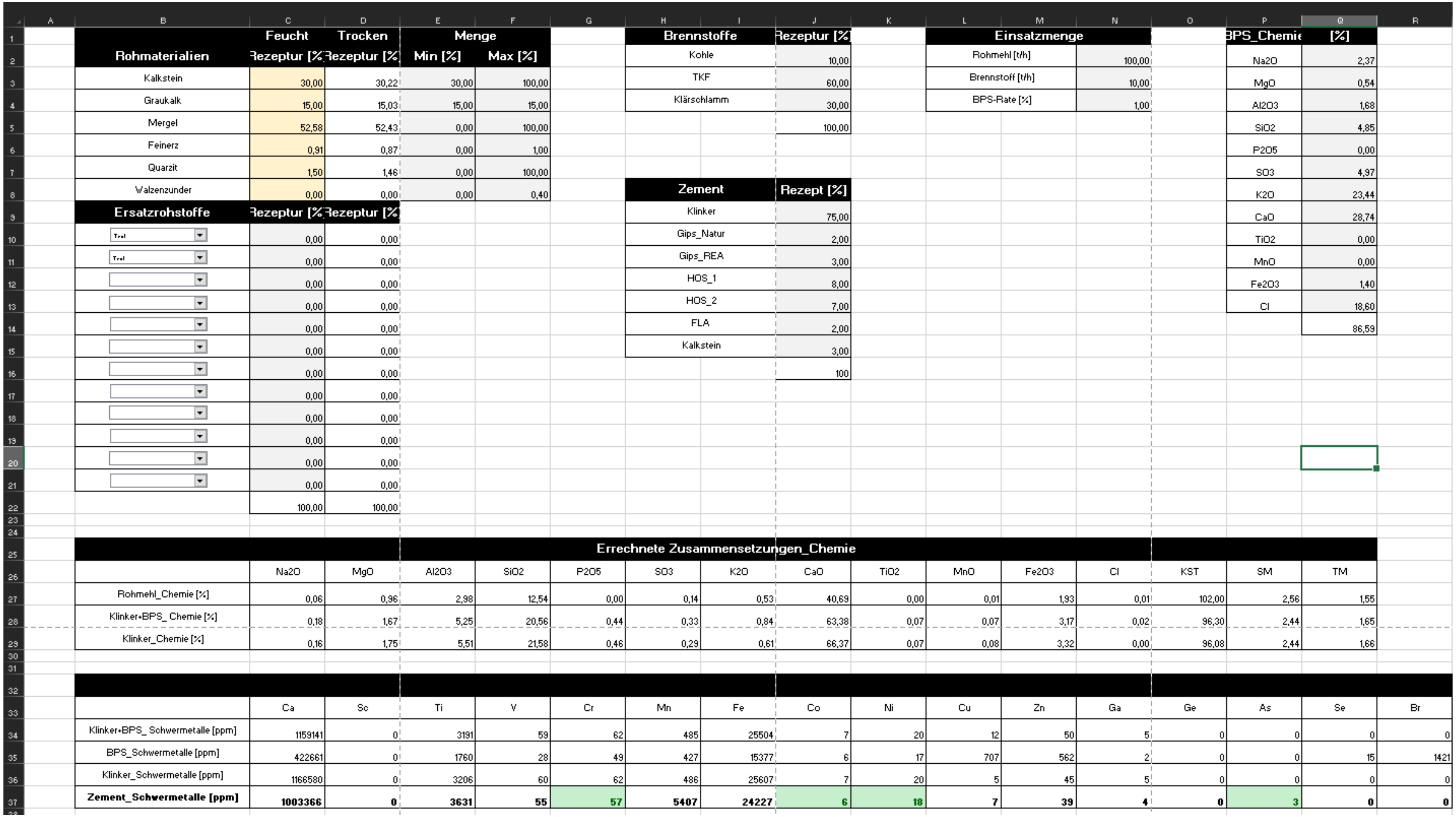
After calculating the two clinker and bypass dust chemistries, one from the raw meal and one from the fuel, these two are added to obtain the entire clinker + bypass dust chemistry by using the ratio of the raw meal (RM) and fuel. The ratio was determined from the amount used as follows:

$$Ratio_{RM} = \frac{RM\left[\frac{t}{h}\right]}{RM\left[\frac{t}{h}\right] + Fuel\left[\frac{t}{h}\right]} \quad (4.2)$$

$$Ratio_{Fuel} = \frac{Fuel\left[\frac{t}{h}\right]}{RM\left[\frac{t}{h}\right] + Fuel\left[\frac{t}{h}\right]} \quad (4.3)$$

The amount [t/h] of the clinker was calculated using the given bypass dust chemistry and the amounts [t/h] of clinker + bypass dust and bypass dust. The resulting clinker chemistry was calculated by percentage calculation. The cement chemistry was then calculated using a recipe consisting of the percentages of clinker, solidification regulator and additives. The calculation of the heavy metals was carried out in the same way. The overview of the created mass balance can be seen in *figure 4.3*.

The analysis behind is decisive for developing a mass balance. It is the basis for every further change, interpretation of the observations and optimization potential. The standard-compliant analysis method for recording the chemical composition and heavy metals is the ICP-OES. Since this analysis method has to be carried out by an external analysis centre and therefore takes a long time to get the results, XRF is used as an alternative analysis method. Therefore, the applicability of the XRF for solid recovered fuels was checked by a round robin test, which is described in the following *section 4.2.*



Rohmaterialien	Feucht Rezeptur [%	Trocken Rezeptur [%]	Menge Min [%]	Max [%]
Kalkstein	30,00	30,22	30,00	100,00
Graukalk	15,00	15,03	15,00	15,00
Mergel	52,58	52,43	0,00	100,00
Feinerz	0,91	0,87	0,00	1,00
Quarzit	1,50	1,46	0,00	100,00
Walzenzunder	0,00	0,00	0,00	0,40

Ersatzrohstoffe	Rezeptur [%	Rezeptur [%]
	0,00	0,00
	0,00	0,00
	0,00	0,00
	0,00	0,00
	0,00	0,00
	0,00	0,00
	0,00	0,00
	0,00	0,00
	0,00	0,00
	0,00	0,00
	0,00	0,00
	0,00	0,00
	100,00	100,00

Brennstoffe	Rezeptur [%]
Kohle	10,00
TKF	60,00
Klärschlamm	30,00
	100,00

Zement	Rezept [%]
Klinker	75,00
Gips_Natur	2,00
Gips_REA	3,00
HOS_1	8,00
HOS_2	7,00
FLA	2,00
Kalkstein	3,00
	100

Einsatzmenge	
Rohmehl [t/h]	100,00
Brennstoff [t/h]	10,00
BPS-Rate [%]	1,00

BPS_Chemie	[%]
Na2O	2,37
MgO	0,54
Al2O3	1,68
SiO2	4,85
P2O5	0,00
SO3	4,97
K2O	23,44
CaO	28,74
TiO2	0,00
MnO	0,00
Fe2O3	1,40
Cl	18,60
	86,59

Errechnete Zusammensetzungen_Chemie

	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	K2O	CaO	TiO2	MnO	Fe2O3	Cl	KST	SM	TM
Rohmehl_Chemie [%]	0,06	0,96	2,98	12,54	0,00	0,14	0,53	40,69	0,00	0,01	1,93	0,01	102,00	2,56	1,55
Klinker+BPS_ Chemie [%]	0,18	1,67	5,25	20,56	0,44	0,33	0,84	63,38	0,07	0,07	3,17	0,02	96,30	2,44	1,65
Klinker_Chemie [%]	0,16	1,75	5,51	21,58	0,46	0,29	0,61	66,37	0,07	0,08	3,32	0,00	96,08	2,44	1,66

	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Klinker+BPS_ Schwermetalle [ppm]	1159141	0	3191	59	62	485	25504	7	20	12	50	5	0	0	0	0
BPS_Schwermetalle [ppm]	422661	0	1760	28	49	427	15377	6	17	707	562	2	0	0	15	1421
Klinker_Schwermetalle [ppm]	1166580	0	3206	60	62	486	25607	7	20	5	45	5	0	0	0	0
Zement_Schwermetalle [ppm]	**1003366**	**0**	**3631**	**55**	**57**	**5407**	**24227**	**6**	**18**	**7**	**39**	**4**	**0**	**3**	**0**	**0**

Figure 4.3: Extract of the established mass balances

4.2 XRF as an alternative method to ICP-OES (round robin test)

Due to the steadily increasing quality requirements for laboratories and the analysis methods used, the need for faster methods with nonetheless equivalent performance characteristics (reproducibility, repeatability, accuracy) compared to external quality controls is also increasing. It is therefore advisable that round robin tests are used for comparative measurements of different analytical methods, as well as for an independent validation of one's own measurement results.

For this reason, the laboratory of the company “w&p Zement GmbH Development/Quality Assurance” took part in the interlaboratory comparison for "Solid recovered fuels - Determination of element composition by X-ray fluorescence according to ISO/NP 22940:2019", offered by the “Federal Environment Agency GmbH”.

The aim of this round robin test was to demonstrate the applicability of the X-ray fluorescence method for various combinations of sample preparation and analysis methods (variants) using three real SRF (solid recovered fuels) samples and to evaluate performance characteristics.

As part of the round-robin test, three real samples of solid recovered fuels (SRF) were selected and distributed to the registered participants. The sample preparation, sample homogenization and particle size reduction of the selected samples was carried out in accordance with EN 15443 and EN 15413 by the Federal Environment Agency (Austrian Environment Agency; Unit Laboratories).

The following *table 4.2* lists the materials used, the different possibilities for sample preparation and analysis methods and the possible settings of the XRF, as well as the elements examined.

Table 4.2: Materials, variants for sample preparation and methods for analysis and analytes of the round robin test.[72]

MATERIAL SOLID RECOVERED FUELS (SRF)	METHOD/VARIANT(S)		
	SAMPLE PREPARATION	ANALYSIS METHOD	TYPE OF X-RAY FLUORESCENCE SPECTROMETER
SRF A: HIGH CALORIFIC WASTE FRACTION FROM NON-HAZARDOUS MUNICIPAL SOLID WASTE; PARTICLE SIZE: <0.5 MM; HETEROGENEOUS MATRIX	cold press and/or hot mould press and/or (powder)	quantitative: Calibration with reference material and/or reference samples and/or semi-quantitative: Fundamental approach (pre-calibrated analytical methods by manufacturer) and/or screening: Fundamental approach	energy dispersive EDXRF and/or wavelength dispersive WDXRF
SRF B: HIGH CALORIFIC WASTE FRACTION FROM COMMERCIAL WASTE; PARTICLE SIZE: <0.5 MM; HETEROGENEOUS MATRIX			
SRF C: MUNICIPAL SEWAGE SLUDGE; FINELY GROUND; HOMOGENEOUS MATRIX			
ANALYTES	Al Aluminium, As Arsenic, Br Bromine, Ca Calcium, Cd Cadmium, Cl Chlorine, Co Cobalt, Cr Chromium, Cu Copper, Fe Iron, K Potassium, Mg Magnesium, Mn Manganese, Mo Molybdenum, Na Sodium, Ni Nickel, P Phosphorus, Pb Lead, Sb Antimony, Si Silicon, Sn Tin, S Sulphur, Ti Titanium, Tl Thallium, V Vanadium, Zn Zinc		

A total of 20 laboratories from 10 countries took part in the round robin test, which registered for a total of 34 variants (sample preparation/analysis methods). The participants could choose from the following options:

Sample preparation techniques:

a) pressed pellets by cold pressing (at least 30 kN)
b) pressed pellets by hot molding press (<180 ° C; at least 30 kN)
c) Powder form (if no other sample preparation technique is available)

Options for determining elements by XRF:

a) quantitative analysis of pressed pellets for main elements (calibration is based on various reference materials and samples of solid fuels with known content)
b) semi-quantitative analysis of pressed pellets for main and secondary elements (the calibration is based on matrix-independent calibration curves that were previously created by the manufacturer)
c) Screening analysis of samples in powder form (semi-quantitative measurement with matrix-independent calibration curves)

The cold press/semi-quantitative variant was used most frequently by the participating laboratories.

Each participant received 50 g per sample and selected variant. For each sample and measurement technique two independent sample preparations as well as a double analysis of the prepared samples by XRF under repeatability conditions according to ISO/AWI TS 22940: 2019 had been carried out by the participations. All relevant information regarding sample preparation, analytical methods/measuring procedures and quality control were also be provided. For the statistical treatment of data, the results obtained was given with at least 3 significant digits and were given in mg/kg$_{DM}$ (105 °C) with the measurement uncertainty for the variant in %.

In addition, control tests were carried out by an in-house labour as well as reference laboratories to assess the homogeneity and stability and to determine the assigned value. For this purpose, random samples of SRF materials A, B and C were made available to the reference laboratories for analysis.

The reference laboratories used to analyse the assigned values for the elements Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, S, Ti, V, Zn, Tl and Sn after the microwave-assisted pressure digestion using hydrofluoric acid (HF), nitric acid (HNO_3) and hydrochloric acid (HCl) the inductively coupled optical plasma emission spectrometry (ICP-OES).

For the determination of the elements Cl and Br, ion chromatography was used after the sample had been burned in a calorimetric vessel. For the determination of sulphur, an additional combustion of the samples at 1150 °C with the addition of WO_3 (elemental analyser) was carried out.

All reference laboratories performed duplicate determinations for each sample and adhered to ISO/IEC 17025. The control tests gave a calculated relative standard deviation for the elements listed in *table 4.3*. The relative standard deviation of <15 % for the determined elements is marked as 'x'. The relative standard deviations >15 % of the elements are shown with the specifically calculated values. No standard deviation could be calculated for As (SRF A, B, C) and Sb (SRF C) (<LOQ), which is marked as '-'. For stability testing the difference

between normalized results for measurements after sample dispatch ‘t2’ and before sample dispatch ‘t1’ was calculated. A difference was lower than 15 % for the elements marked with 'xx' in the *table 4.3*.

Table 4.3 shows the relative standard deviation of the control tests by the reference laboratories and the results of the stability testing. A relative standard deviation below 15 % is marked as ‘x’. If no standard deviation could be calculated, it is marked with ‘-‘. Was the difference for the stability testing lower than 15 % it is marked with ‘xx’.

ELEMENT	RELATIVE STANDARD DEVIATION [%]			STABILITY TEST		
	SRF A	SRF B	SRF C	SRF A	SRF B	SRF C
Al	x	x	x	xx	xx	xx
As	-	-	-			
Ca	x	x	x	xx	xx	xx
Cd	x	40	x	xx	xx	xx
Co	x	18	x	xx	xx	
Cr	x	x	x	xx	xx	
Cu	75	95	x			xx
Fe	x	x	x	xx	xx	xx
K	x	x	x	xx	xx	xx
Mg	x	x	x		xx	xx
Mn	x	44	x	xx		xx
Mo	16	27	x	xx	xx	
Na	x	x	x		xx	
Ni	x	23	x		xx	xx
P	x	x	x	xx	xx	xx
Pb	x	x	x		xx	xx
Sb	46	18	x	xx		
Si	x	x	x			
S	x	x	x	xx	xx	xx
Ti	x	x	x	xx	xx	xx
V	x	x	x	xx	xx	xx
Zn		x	x			xx
Sn	x	x	x	xx		

All samples were well characterized by internal tests and from the results of the reference laboratories. On the basis of previous experience with SRF samples and on the basis of the standard deviations from the reference analysis using ICP-OES of the analysed elements, the criterion for the evaluation of the round robin test was set at 30 %.

The recovery rate and the z-score were calculated as criteria for performance evaluation. The reference value or assigned value calculated by the reference laboratories after removing outliers was used as the basis for calculating the recovery rate and z-score. The following equations 4.4 and 4.5 were used:

$$recovery\ rate = \frac{\bar{x}_i * 100}{\bar{X}} \qquad (4.4)$$

$\bar{x}_i$ … calculated mean of the participating laboratory
$\bar{X}$ … assigned value

$$z - score = \frac{\bar{x}_i - \bar{X}}{criteria} \qquad (4.5)$$

$\bar{x}_i$ … calculated mean of the participating laboratory
$\bar{X}$ … assigned value
criteria … For this interlaboratory testing the criteria was defined by expert judgement and set for 30 % of the assigned value by reference laboratories.

As an example, the recovery rate and the z-score are calculated for the element aluminium of the sample SRF A (LC0034):

$\bar{x}_i = 25300$ mg/kg$_{DM}$

$\bar{X} = 30210$ mg/kg$_{DM}$

$$criteria = 30210\, mg/kg_{DM} * 30\,\% = 9063\, \mathrm{mg/kg}_{DM}$$

$$recovery\ rate = \frac{25300\, mg/kg_{DM} * 100}{30210\, mg/kg_{DM}} = 84\,\%$$

$$z - score = \frac{25300\, mg/kg_{DM} - 30210\, mg/kg_{DM}}{9063\, mg/kg_{DM}} = -0{,}5$$

Therefore, a value of 84 % for recovery rate and -0,5 for the z-score is calculated.

The following ratings were used for the interpretation of the recovery rate and the Z-Score:

Interpretation of recovery rate:

- Recovery rate between 70 % - 130 % → good result
- Recovery rate between 40 % - 160 % → satisfactory result
- Recovery rate lower than 40 % or higher than 160 % → unsatisfactory result

Interpretation of z-scores:

- |z-score| ≤ 1.0 → good result
- |z-score| ≤ 2.0 → satisfactory result
- 2.0 < |z-score| < 3.0 → questionable result
- |z-score| ≥ 3.0 → unsatisfactory result

The evaluation of the data for validation of the XRF method was carried out according to ISO 5725-2. Outliers were determined in accordance with ISO 5725-2 (Grubbs test) and after a plausibility check, outliers were eliminated for statistical treatment. Repeatability and reproducibility were calculated according to ISO 5725-2. The complete data set for each variant can be found in the tables in the appendix to ISO document of 22940.

The *figure 4.4* summarizes for each element, if validation data for XRF for the specific variant is in good agreement with results determined by reference laboratories. If the recovery rate falls between 70-130 % it is shown by mark '++' in the following *figure 4.4*

Ele-ment	**Variant**															**remarks**
	Cold press /quantitative			**Hot mould press /quantitative**			**Cold press /semi-quantitative**			**Hot mould press /semi-quantitative**			**Powder /semi-quantitative**			
SRF->	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**	
Al			++	++	++	++			++			++		++	++	
As				++												< LOQ
Br					++		++	++			++		++			< LOQ 100; N=1 (Reflab)
Ca	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	
Cd	++	++	++	++	++	++				++	++	++			++	
Cl	++	++		++	++				++	++		++	++	++		N=1 (Reflab)
Co							++			++	++					
Cr	++	++		++	++	++	++	++	++	++	++	++	++	++		
Cu			++						++			++				High variability (Reflab), metallic particles; XRFlab good comparable results
Fe	++	++	++		++		++		++			++		++	++	
K	++	++	++		++	++	++	++	++	++	++				++	SRF A, high variability (Reflab)
Mg	++	++	++		++	++	++	++	++	++	++				++	
Mn	++		++			++			++			++			++	SRF B, high variability (Reflab)
Mo		++	++			++					++	++				Mo < LOQ SRF A, B, C (Reflab)
Na				++	++	++		++	++	++	++			++	++	SRF A Na high variability (Reflab)
Ni			++	++			++		++			++	++	++		SRF A and SRF B high variability (Reflab), metallic particles; good comparability between XRF results
P	++	++	++					++	++	++	++	++			++	
Pb	++	++	++	++	++				++	++	++	++	++		++	
S	++	++	++	++	++	++	++	++		++	++	++			++	
Sb				++	++		++	++								SRF C Sb < LOQ (Reflab); (Sb < LOQ
Si			++			++									++	SRF A, B, C high variability (Reflab);
Sn			++	++	++				++			++	++			SRF C high variability (Reflab); metallic particles
Ti	++	++	++			++	++	++	++	++	++	++	++			
Tl		(++)								(++)	(++)					SRF A, SRF B < LOQ (Reflab); SRF C high variability between reflab (<0.3 – 4)
V	++	++	++		++				++		++	++				
Zn		++	++		++	++		++	++		++	++	(++)	++	++	SRF A high variability between reflab; metallic particles

Figure 4.4 shows which variants and methods are suitable for analysing the individual elements using XRF. If the recovery rate is between 70-130 % it is shown by mark '++'. [72]

In summary, the evaluation of the data from the interlaboratory comparison shows that XRF can be used as a comparison method to ICP-OES. In some cases, there were high standard deviations for the element content, which was expected in real samples of SRF because of the rather heterogeneous matrices such as samples SRF A and SRF B have. The accuracy of the results could be increased by a matrix-specific calibration, but most of the participants used a matrix-specific calibration just for a few elements (e.g. As, Br, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sn, V, Zn).

The company "w&p Zement" not only acted as a participating laboratory in the interlaboratory comparison, but also as the XRF reference laboratory. As the reference laboratory, the samples SRF A, B and C were prepared using cold press and hot mould press and each pressed tabled was analysed quantitatively (Protrace (I)/Omnian & calibration with standards (II)) and semi-quantitative (precalibrated by manufacturer) with a wavelength dispersive XRF (Rh, 2400W; vacuum, spinner on).

The best results for sample preparation of the samples SRF A and B were obtained by the hot mould press method. For the cold press method, a large amount of wax had to be used. In addition, homogenization was difficult to perform and expansion occurred after pressing. For sample SRF C, both methods yielded good results. The following elements of samples SRF A, B and C were analysed with the respective measurements with acceptable results:

Cold press/quantitative:

- SRF A: Cl, Cr, Fe, K, Mn, Pb, Sb, Ti
- SRF B: Cd, Cl, Cr, Fe, Pb, Sb, Sn, Ti, Zn
- SRF C: Al, Ca, Cd, Cr, Cu, Fe, K, Mn, Mo, Ni, P, Pb, S, Sn, Ti, V, Zn

Hot mould press/quantitative I & II:

- SRF A (I): Al, As, Ca, Cd, Cl, Co, Fe, K, Mn, Na, P, Pb, S, Sb, Sn, V
- SRF A (II): Al, Ca, Fe, K, Mg, Na, P, S, Ti
- SRF B (I): Al, Br, Ca, Cd, Cl, Co, Cr, Fe, K, Mo, Na, P, Pb, S, Sb, Sn, Ti, Tl, Zn
- SRF B (II): Al, Ca, Fe, K, Mg, Na, P, S, Ti
- SRF C (I): Al, Ca, Cd, Cr, Cu, Fe, K, Mn, Mo, Ni, P, Pb, S, Sn, Ti, V, Zn
- SRF C (II): Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti

Cold press/semi-quantitative:

- SRF A: Cr, Mn, P, Pb, Tl, V
- SRF B: Cd, Cr, Pb, Ti, Tl, Zn
- SRF C: Cd, Cl, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn

Hot mould press/semi-quantitative:

- SRF A: As, Ca, Cd, Cl, Co, Cr, K, Mg, Na, P, Pb, S, Ti, Tl
- SRF B: Br, Ca, Cd, Co, Cr, K Mg, Na, P, Pb, S, Sn, Ti, V, Zn
- SRF C: Cd, Cl, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn

The hot mould press/quantitative variant performed best of all variants.

As a participating laboratory, the samples were produced and measured in the same way as for the reference laboratory. A laboratory code was assigned for each variant as follows:

- LC0030 → cold press / quantitative
- LC0031 → hot mould press / quantitative I
- LC0032 → cold press / semi-quantitative
- LC0033 → hot mould press / semi-quantitative
- LC0034 → hot mould press / quantitative II

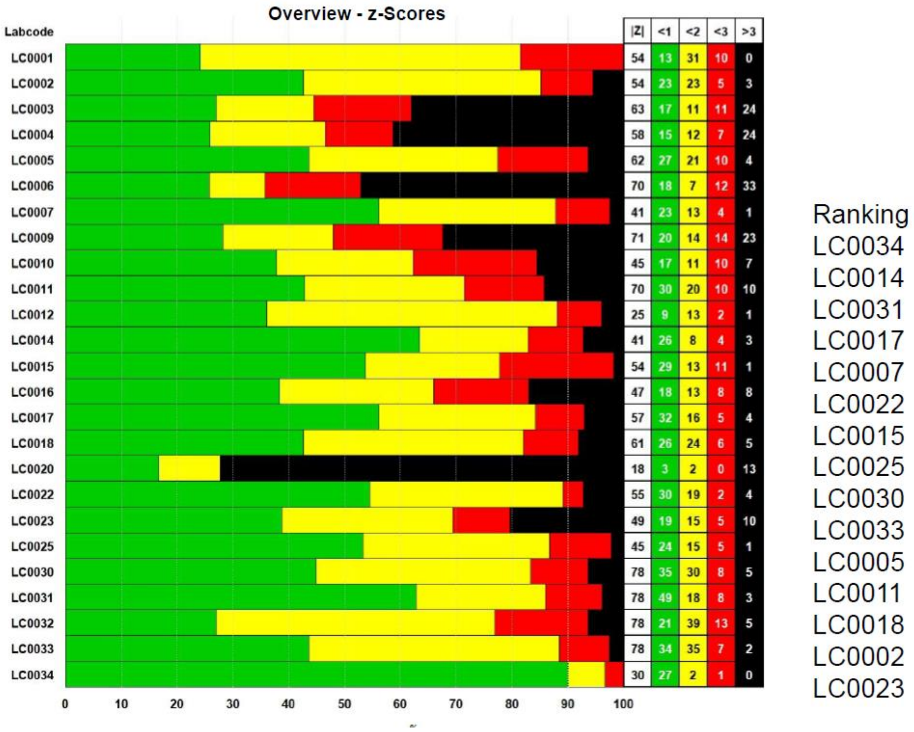


Figure 4.5: Overview of all XRF results using the determined z-scores.[72]

As can be seen in *figure 4.5*, the company "w&p Zement" achieved the best results in the interlaboratory comparison with the variant hot mould press / quantitative II (LC0034). The variants hot mould press / quantitative I (LC0031), cold press / quantitative (LC0030) and hot mould press / semi-quantitative (LC0033) are also represented in the top 10.

The information and data of the round robin test was taken from the draft report "Interlaboratory Comparison for Solid recovered fuels – Determination of elemental composition by X-ray fluorescence (ISO/NP 2294:2019) SRF 19XRF". [72]

4.3 Optimization potential through improved calibration for alkalis, chloride and sulphur and error analysis

In order to be able to reliably control the product quality and the process stability at all times, the development and use of a material flow balance is highly recommended. However, the correct recording of the alkali, chloride and sulphur contents entered via secondary raw materials, secondary fuels and other input materials and discharged by bypass dust and clinker is an absolute prerequisite for an accurate informational value of this material flow balance. In addition, the analytics used must meet the requirements for analysis speed and resource-saving sample handling (e.g. sample preparation with little effort). The XRF is therefore a promising analyser for these tasks. When using XRF as an analysis method, a factory-specific calibration of the elements under consideration is necessary for correct recording. The preparation of the calibration was described in *section 3.2.5*.

The following *table 4.4,* which summarizes all correlation factors, serves as an overview of the results of the individual calibrations. To be able to interpret the results more easily, a few examples of the calibrations are shown as an image and described in more detail. The remaining figures of the individual calibrations are attached in the *appendix v.*

Table 4.4: Correlation factors of the individual calibration lines for bypass dust, raw stone (limestone + marl), kiln inlet, hot meal and clinker for potassium (K), sodium (Na), sulphur (SO_3) and chloride (Cl) with and without the newly produced mixed samples (MS). The meaning of the abbreviations is as follows: D… value of intercept; E ... slope for calibration line; RMS… standard deviation; RE… relative error; K… K factor (constant). F… quadratic term of the calibration line is fixed at zero and is therefore not given in table.

BYPASS DUST

CALIBRATION	D	E	RMS	RE	K	CORRELATION
BPS_K	-2.888	0.022	0.581	0.040	0.151	0.943
BPS_K_MS	-0.024	0.019	0.592	0.041	0.155	0.976
BPS_Na	0.190	0.050	0.160	0.101	0.126	0.733
BPS_Na_MS	0.074	0.038	0.250	0.083	0.141	0.972
BPS_SO_3	0.545	0.022	0.216	0.050	0.103	0.962
BPS_SO_3_MS	0.317	0.023	0.339	0.062	0.144	0.944
BPS_Cl	-6.787	0.037	1.002	0.086	0.293	0.847
BPS_Cl_MS	-4.554	0.033	0.715	0.054	0.194	0.995
LIMESTONE + MARL						
KS+ME_K	-0.065	0.011	0.046	0.054	0.043	0.996
KS+ME_K_MS	-0.065	0.011	0.044	0.052	0.042	0.997
KS+ME_Na	0.041	0.007	0.004	0.023	0.010	0.876
KS+ME_Na_MS	-0.051	0.057	0.019	0.051	0.029	0.995
KS+ME_SO_3	0.032	0.010	0.026	0.136	0.059	0.918
KS+ME_SO_3_MS	0.028	0.008	0.034	0.165	0.073	0.859
KILN INLET						
OE_K	0.002	0.011	0.009	0.012	0.011	0.996
OE_K_MS	-0.023	0.011	0.012	0.015	0.013	0.995
OE_Na	-0.023	0.045	0.006	0.033	0.014	0.991
OE_Na_MS	-0.042	0.052	0.015	0.057	0.028	0.993
OE_SO_3	-0.043	0.015	0.037	0.113	0.064	0.881
OE_SO_3_MS	-0.068	0.022	0.058	0.140	0.087	0.987
OE_Cl	-0.021	0.024	0.005	0.046	0.016	0.983
OE_Cl_MS	-0.012	0.019	0.008	0.054	0.020	0.990
HOT MEAL						
HM_K	-0.009	0.014	0.114	0.031	0.059	0.982
HM_K_MS	-1.464	0.026	0.174	0.031	0.073	0.993
HM_Na	0.014	0.059	0.063	0.122	0.086	0.920
HM_Na_MS	-0.030	0.066	0.091	0.098	0.087	0.994
HM_SO_3	-0.146	0.022	0.062	0.046	0.053	0.972
HM_SO_3_MS	-0.346	0.025	0.120	0.053	0.075	0.996
HM_Cl	0.047	0.024	0.062	0.025	0.039	0.991
HM_Cl_MS	-0.015	0.025	0.182	0.064	0.107	0.936
CLINKER						
KLI_K	-0.027	0.011	0.017	0.024	0.020	0.995
KLI_K_MS	-0.024	0.014	0.013	0.010	0.011	0.999
KLI_Na	0.105	0.026	0.011	0.031	0.019	0.930
KLI_Na_MS	0.029	0.040	0.027	0.061	0.040	0.994
KLI_SO_3	-0.000	0.020	0.051	0.081	0.064	0.915
KLI_SO_3_MS	-0.017	0.020	0.053	0.075	0.062	0.984
KLI_Cl	-0.000	0.018	0.008	0.060	0.022	0.948
KLI_Cl_MS	-0.011	0.024	0.011	0.065	0.026	0.997

Figure 4.6 shows the calibration line for sodium of the clinker samples. On the top is the calibration line with the newly calibrated mixed samples and at the bottom the calibration without the mixed samples. The red markings in the lower graph are the measurements of the new composite samples, which are not taken into account in this calibration. Basically, only the green markings and not the red markings are included in the calibration. A clear increase in the concentration range can be seen here. The old calibration line was only in the concentration range of about 0.2-0.3 %, whereas the new calibration line covers a range of about 0.2-1.1 %. As it can also be seen in *table 4.4*, the correlation increases with the new calibration from 0.930 to 0.994, which is a significant improvement.

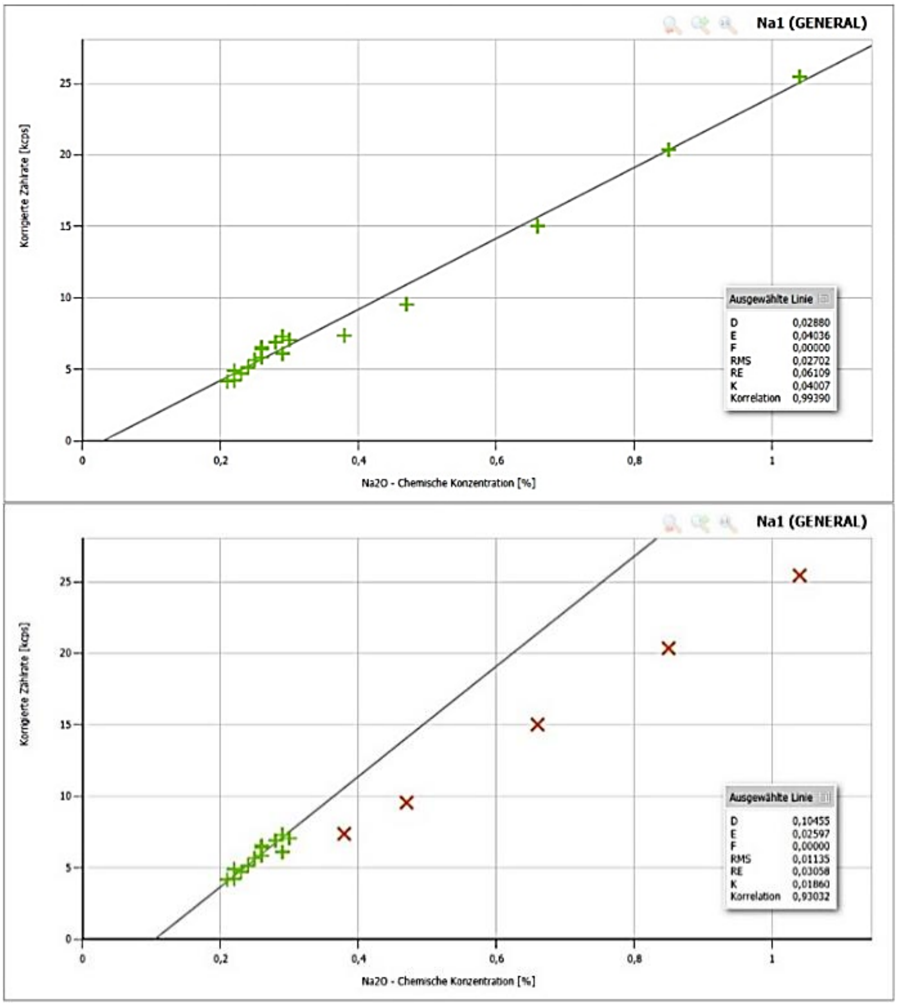


Figure 4.6: Calibration line for sodium from the clinker samples (upper graph with new mixed samples, lower graph without mixed samples). The chemical concentration of Na_2O in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis.

The calibration line for potassium of the raw stone samples (limestone and marl) was also slightly improved by the mixed samples. As can be seen in *figure 4.7*, the concentration range has been increased slightly to a range of about 0-1.8 % and the correlation has been raised from 0.996 to 0.997. The already high correlation of almost 1 show, however, that the original correlation already fit very well. In this case, the inclusion of the mixed samples in the calibration serves more as an internal check for the correctness of the previous measured values and as their extension of the concentration range.

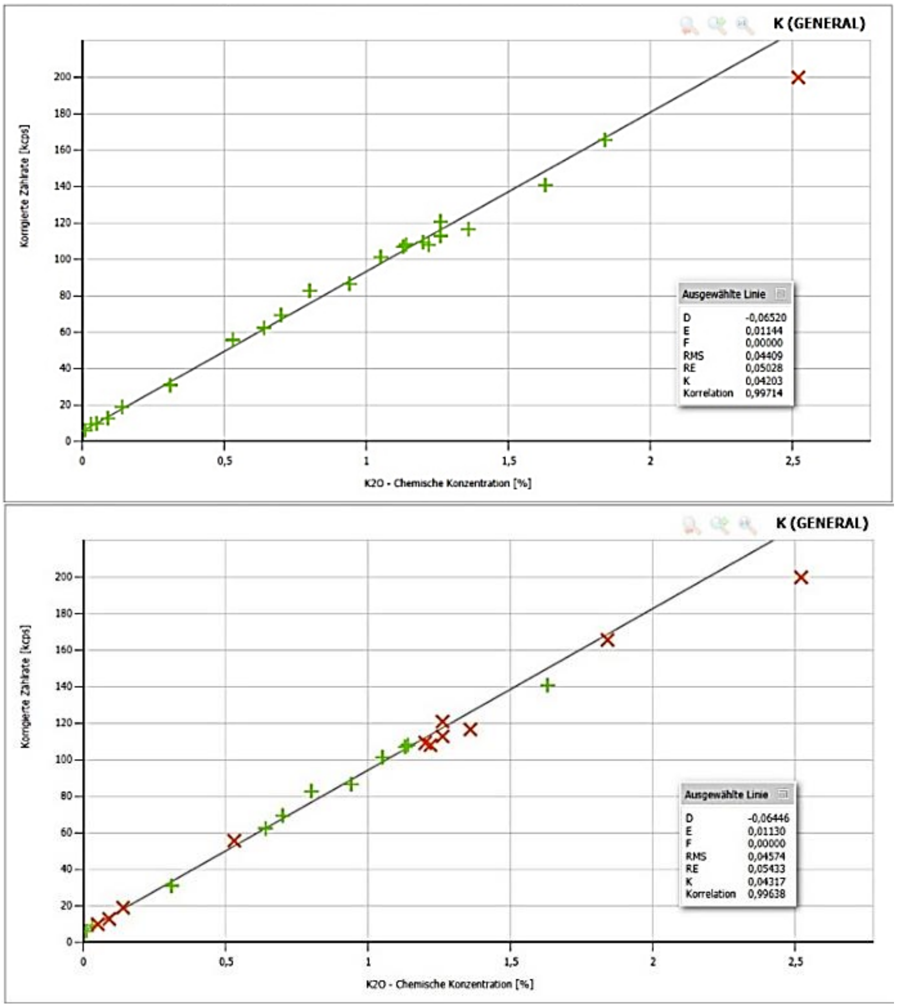


Figure 4.7: Calibration line for potassium from the raw stone samples (upper graph with new mixed samples, lower graph without mixed samples). The chemical concentration of K_2O in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis.

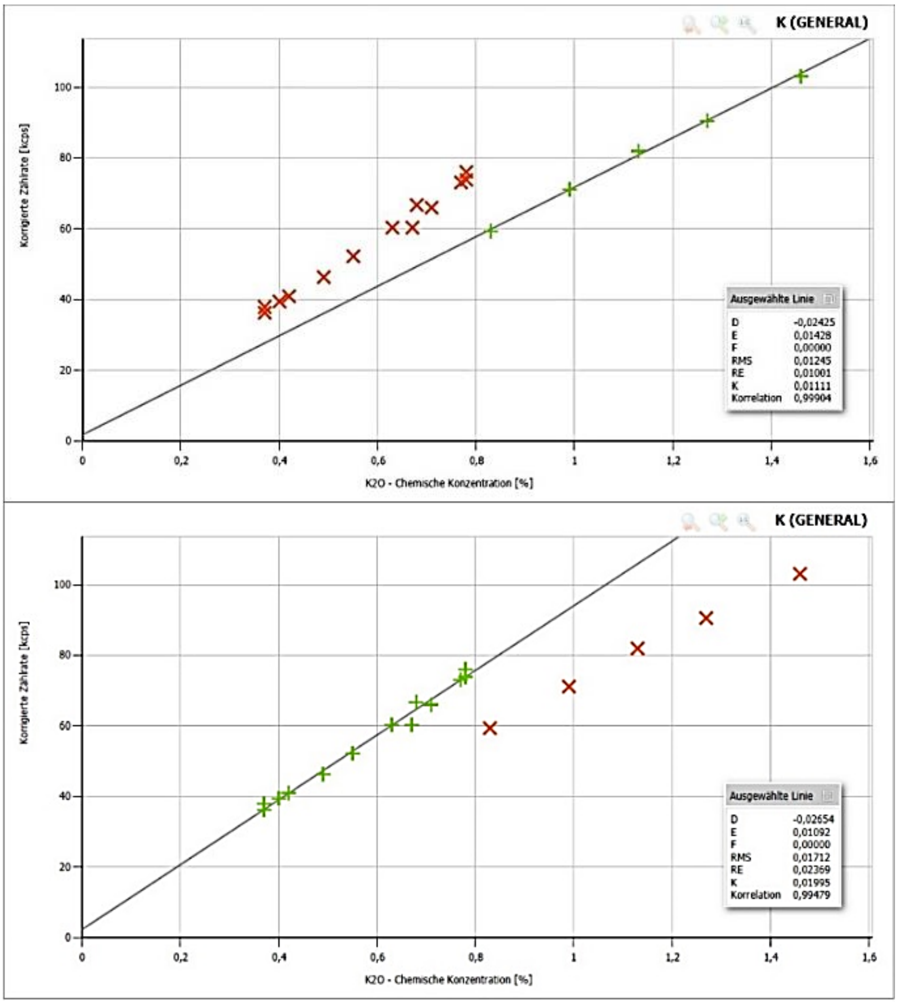


Figure 4.8: Calibration line for potassium from the clinker samples (upper graph with new mixed samples, lower graph without mixed samples). The chemical concentration of K_2O in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis.

Figure 4.8 shows the calibration lines for potassium from the clinker samples with the mixed samples (top) and without the mixed samples (bottom). In this case it becomes clear that the new calibration line does not match the old one and is shifted slightly downwards. It seems that with the old calibration line a systematic under-determination of the potassium content of the sample took place. Due to the change in personnel and analysis equipment, there is an uncertainty as to how these standards were produced and measured, but it can be assumed that the old standards were measured with the XRF using an orodispersible tablet. Melting the material reduces existing matrix effects, which are explained in *section 2.4.4.1*, but the high temperature also means that volatile elements such as potassium at least partially evaporate, which in this case seems to be the reason for the under-determination of the potassium content. However, since the alkaline input was kept relatively low in the past, this calibration was not renewed immediately. With the increased use of substitute raw materials, and thus a higher input of alkalis, the focus was now on renewing the alkaline calibration. The correlation of the new calibration line has also slightly improved from 0.995 to 0.999. The concentration range was increased from 0.4-0.8 % to 0.8-1.5 %, which appears to be suitable for the higher alkali input. The error that leads to the systematic shifting of the curve, could also lie in the external determination of the reference value via ICP-OES, which is the initial sample for the mixed samples. In the following example, this error of the reference value analysis is shown in detail.

Figure 4.9 shows the new calibration for potassium from the hot meal samples with the mixed samples (top) and the old calibration without mixed samples (bottom).

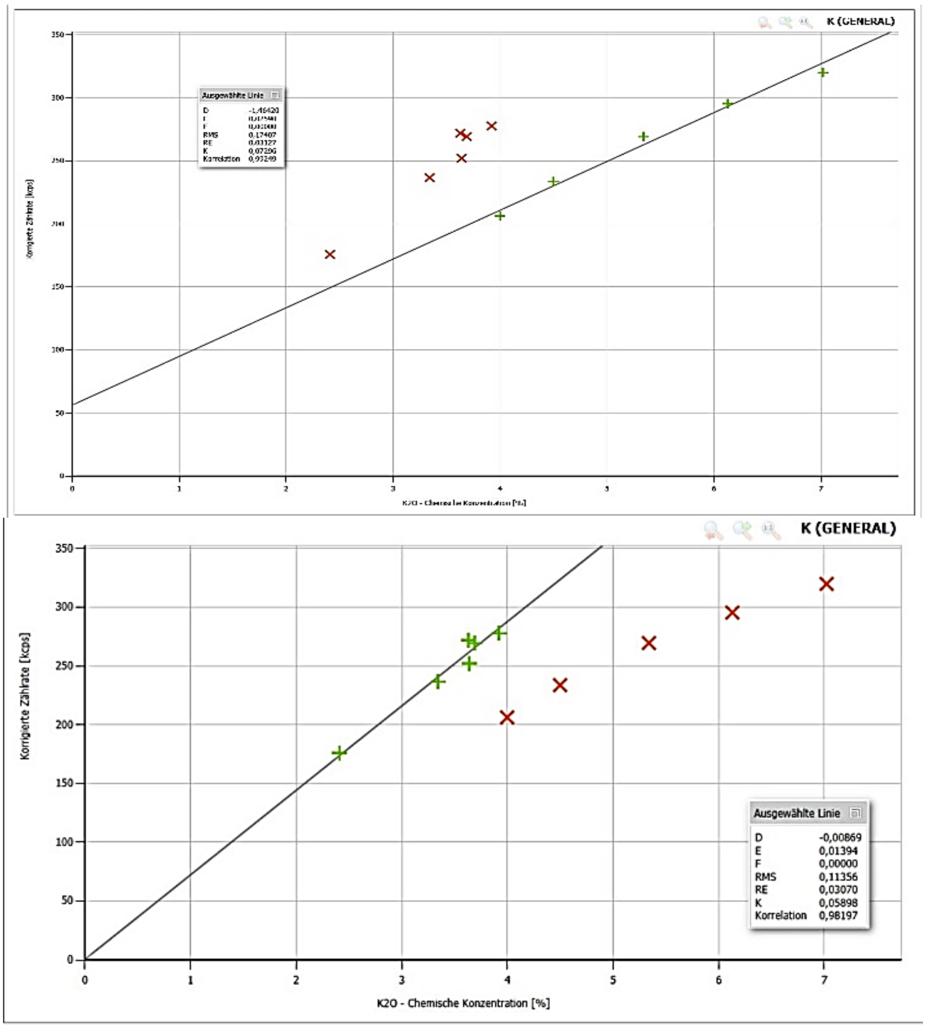


Figure 4.9: Calibration line for potassium from the hot meal samples (upper graph with new mixed samples, lower graph without mixed samples). The chemical concentration of K_2O in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis.

Also in this case, it seems to be an under-determination of the potassium content in the historical calibration and also two separate curves can be clearly seen. It can also be seen that the calibration line of the new mixed samples intersects the x-axis at -1.464 %, which is relatively far off the zero point. One reason for this could be that, compared to the potassium calibration of the clinker, there are significantly higher concentrations in the potassium calibration of hot meal (0.4-1.2 % vs. 2-7 %). It is therefore possible that the new calibration is correct for the concentration range under consideration, but that the calibration does not behave linearly over the entire concentration range (towards lower concentrations). This means that it can be neglected that the straight line does not go through the zero point.

To check why the calibration lines are shifted, some standards were sent to the reference laboratory for analysis using ICP-OES for a second time. For example, the following K_2O values, seen in *table 4.5*, were determined from the same reference sample of the bypass dust with the same external determination using ICP-OES at two different times:

Table 4.5: Results of the K_2O reference analysis using ICP-OES for the bypass dust reference sample (standard 14) at two different execution times.

SAMPLE	K_2O [%]
BPS STD. 14 (1. ANALYSIS) – USED AS BLIND SAMPLE IN CALIBRATION SEEN IN FIGURE 4.12	15.70
BPS STD. 14 (2. ANALYSIS)	13.30

The analyses of potassium of the same reference sample from the bypass dust carried out at a different point in time show a deviation of 2.4 %, which establishes a shift in the calibration curves. Since the establishment of the calibration line is based on the external analyses of the reference samples from the process samples used, systematic errors can occur due to the high fluctuations in the external analysis results using ICP-OES. The reason for the fluctuations can be found in the preparation of the sample for the measurement using ICP-OES. A highly diluted measurement solution (around 0.004 g/ml) is prepared with a small amount of sample (around 0.2 g). Due to the relative inhomogeneity of the real process samples, a high level of representativeness cannot be achieved. The higher the concentration of the process samples, the bigger the dilution error, which means that the reference analysis of the alkali content is not suitable.

Another possibility of how systematic differences in the calibrations can result from pure process samples and mixed process samples, as seen in *figure 4.9*, are matrix effects. However, matrix effects can often be reduced by increasing the sample fineness. In order to obtain an indication of whether matrix effects occurred in the measurement of the mixed samples produced, different milling times were compared with one another during sample preparation.

In addition, it can be assumed that different chemicals also cause a different matrix effect, should this be significant. Therefore, different chemicals (KCl/K_2SO_4 or $Na_2SO_4/NaCl$) were used to set the desired potassium or sodium content, in order to be able to assess the extent of an existing matrix effect. The results are shown in the following *table 4.6* and *table 4.7.*

Table 4.6: Chemicals used, calculated K_2O values and analysed K_2O values at different grinding times for the mixed samples of bypass dust.

BYPASS DUST

SAMPLE	CHEMICALS	K_2O [%]			
		CALCULATED VALUE	GRINDING TIME 45S	GRINDING TIME 70 S	GRINDING TIME 95 S
BPS BP	-	15.78	14.03	14.23	14.04
BPS P1	KCl	17.31	15.33	15.48	15.52
BPS P2	KCl_GROUND	17.31	15.75	15.62	15.94
BPS P3	$KHSO_4$	16.86	15.48	15.87	15.30
BPS P4	K_2SO_4_GROUND	20.76	18.03	17.76	18.19
BPS P5	K_2SO_4	20.76	17.68	17.88	17.56

Table 4.7: Chemicals used, calculated K_2O values and analysed K_2O values at different grinding times for the mixed samples of limestone, marl, kiln inlet, hot meal and clinker.

LIMESTONE

SAMPLE	CHEMICALS	K_2O [%]		
		CALCULATED VALUE	GRINDING TIME 30 S	GRINDING TIME 90 S
KS BP	-	0.05	0.03	0.03
KS P1	KCl/Na_2SO_4	0.52	0.58	0.58
KS P2	KCl/NaCl	0.52	0.64	0.58
KS P3	K_2SO_4/Na_2SO_4	0.98	1.20	1.18
KS P4	K_2SO_4/NaCl	0.98	1.20	1.20

MARL

SAMPLE	CHEMICALS	K_2O [%]		
		CALCULATED VALUE	GRINDING TIME 30 S	GRINDING TIME 90 S
ME BP	-	1.20	1.07	1.08
ME P1	KCl/Na_2SO_4	1.59	1.42	1.40
ME P2	KCl/NaCl	1.59	1.42	1.41
ME P3	K_2SO_4/Na_2SO_4	1.97	1.80	1.80
ME P4	K_2SO_4/NaCl	1.97	1.80	1.82

KILN INLET

SAMPLE	CHEMICALS	K_2O [%]		
		CALCULATED VALUE	GRINDING TIME 30 S	GRINDING TIME 90 S
OE BP	-	0.75	0.74	0.79
OE P1	KCl/Na_2SO_4	0.87	0.95	0.94
OE P2	KCl/NaCl	0.87	0.93	0.94
OE P3	K_2SO_4/Na_2SO_4	1.00	1.18	1.16
OE P4	K_2SO_4/NaCl	1.00	1.16	1.17

HOT MEAL

SAMPLE	CHEMICALS	K_2O [%]		
		CALCULATED VALUE	GRINDING TIME 45 S	GRINDING TIME 100 S
HM P1	K_2SO_4/Na_2SO_4	4.91	3.78	3.77
HM P2	K_2SO_4/NaCl	4.91	3.78	3.78

CLINKER

SAMPLE	CHEMICALS	K_2O [%]		
		CALCULATED VALUE	GRINDING TIME 60 S	GRINDING TIME 120 S
KLI P1	K_2SO_4/Na_2SO_4	1.48	1.14	1.12
KLI P2	K_2SO_4/NaCl	1.48	1.13	1.17

When comparing the K_2O and Na_2O values in relation to the grinding time, only small differences are visible, so matrix effects due to the shorter grinding time can be excluded. Even when comparing the chemicals used, no major differences can be observed. From this it can be concluded that the chemicals used and the grinding time do not seriously affect the measurement results.

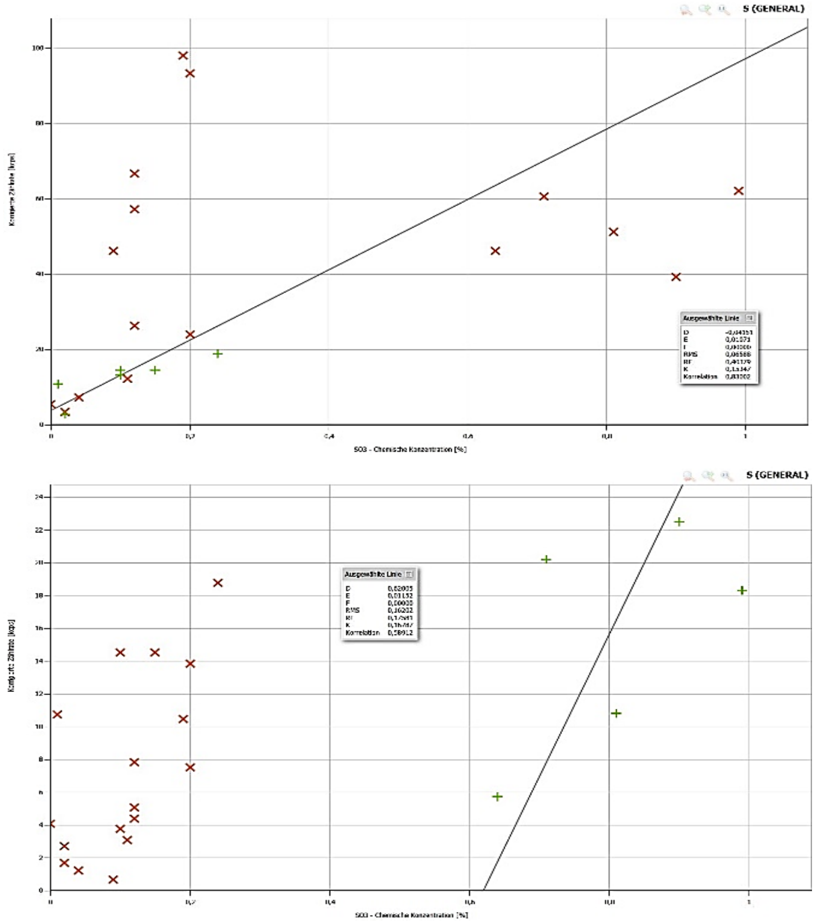


Figure 4.10: Calibration line for sulphur from the raw stone samples (upper graph with new mixed samples of limestone, lower graph with new mixed samples of marl). The chemical concentration of SO_3 in percent is plotted on the x-axis and the corrected counting rate in kcps is plotted on the y-axis.

An example of how strong the matrix effects can be, is shown in *figure 4.10*, which shows the raw stone calibration for sulphur with limestone and marl samples that have the same sulphur concentration. The green markings in the figure on the top show the reference and mixed samples of limestone, whereas the green markings in the lower figure show the blind and mixed samples of marl. The other measured values marked in red in *figure 4.10* come from measurements of other raw stone standards. However, these are not taken into account in this discussion. Due to the different sample matrix of limestone and marl, the measurement results are significantly shifted. For the raw stone calibration, an attempt was made to integrate the different quarry materials, i.e. limestone, grey limestone and marl, together into the calibration. However, because of the strong matrix effects, it would make sense to carry out the raw stone calibration separately for the individual materials.

5 Conclusion and Outlook

In order to be able to manage the upcoming changes in the cement industry to achieve the goal of becoming climate neutral by 2050 in a target-oriented manner, a stable process of cement production is required as a basis. In order to ensure a stable process, various factors, such as chemical, procedural, legal and economic aspects, which are of great importance for cement production, must be reconciled. For this purpose, within the scope of this master's thesis, a mass balance was developed as a tool for the targeted handling of the challenges and for the determination and evaluation of the optimal process flow over the entire cement production process. The mass balance offers the possibility to calculate the optimal raw meal, fuel and additive composition for the production of the best possible cement quality, as well as the compliance with the legal limit values, e.g. for heavy metals. Furthermore, a targeted control of the firing process or kiln status is enabled instead of reacting to negative process observations afterwards. This can reduce disruptions in the process flow and consequently process standstills, which in turn has a positive effect on the economic aspects of cement production.

Fundamental for the development of the mass balance and for the understanding of the complex interplay of the different challenges and their effects on the process is the underlying analytics as a basis for assessment. The results of the analytical investigations not only serve as input variables for the material balance, but are also used for correlation with process parameters and thus for building a deeper process understanding.

A fast and reliable analysis method is required for the process-related investigation. For this reason, X-ray fluorescence analysis is used at the Wietersdorf plant as an alternative method to optical emission spectroscopy with inductively coupled plasma. In order to check the applicability of XRF for heavy metal analysis of substitute fuels as an alternative analysis method to ICP-OES, the company “w&p Zement GmbH” took part in the round robin test "Solid recovered fuels - Determination of element composition by X-ray fluorescence according to ISO/NP 22940:2019". Three real samples of solid recovered fuels (SRF A, B and C) were prepared with two different sample preparation methods (cold pressing and hot moulding) and measured with two analytical methods (semi-quantitative and quantitative) using XRF. In summary, the evaluation of the data from the interlaboratory comparison showed that XRF can be used as an alternative to ICP-OES and that matrix-specific calibration increases the accuracy of the results. The company “w&p Zement GmbH” was able to achieve the best results of the analysis in comparison to the reference analysis ICP-OES with the variant hot moulding/quantitative.

The chemical focus of the work was to completely revise the calibrations of the XRF of the process samples (raw stone, raw meal, hot meal, clinker and bypass dust) for sodium, potassium, chloride and sulphur, in order to gain a better understanding of the process flow and their challenges due to the formation of alkali, chloride and sulphur cycles and consequently formation of deposits and rings in the kiln. The necessary renewal of the calibrations is based on the fact that only measurements that are within the calibration range achieve a correct value. Before the intensification of the use of substitute fuels and substitute raw materials, the provisions of alkalis, chlorides and sulphur were of less importance. The main focus of the XRF calibrations was therefore on a broad measuring range of the main elements. However, the analysis of the main elements alone is no longer sufficient, which means that the calibration range for alkalis, sulphur and chloride must be significantly expanded.

The use of process samples with a wide range of alkali, chloride and sulphur ranges would be ideal for recalibration, but the availability of such process samples is very limited. Therefore, targeted admixtures of alkali chloride or alkali sulphur compounds in the process samples were used as standards. For this purpose, one reference sample and four mixed samples with different amounts of Na_2SO_4 and KCl added were measured for each material type and plotted against the calculated concentration. As a result, the calibrations of raw material, raw meal, hot meal, bypass dust and clinker were clearly improved by using the mixed samples as standards. In addition to the increased concentration range of the calibration, also the correlation, i.e. the relationship between the measured and calculated values of the standards, which should be close to 1, was improved. For example, for the sodium calibration of clinker, an increase in the concentration range from 0.2-0.3 % to 0.2-1.1 % has been achieved. The correlation of the calibration line was raised from 0.930 to 0.994.

In order to clarify why with some calibrations, such as the potassium calibration of hot meal, two different curves were achieved (the calibration lines of historical standards and new mixed samples did not match), further samples were sent to the company “Wessling GmbH” reference laboratory to examine the alkali content using ICP-OES. The duplicate determinations of individual samples, for example the reference sample of bypass dust, gave significantly different results. The difference in the analysis results of the blind sample of bypass dust for potassium is 2.4 %. A deviation of this order of magnitude also causes the shift in the calibration line, which means that the reference analysis of the alkali content with higher concentration is not suitable.

Another reason for the deviation are possible matrix effects of the mixed samples. To check whether matrix effects occur with regard to the sample preparation and the grinding time for the production of the pressed tablets for the measurement using XRF, grinding tests were carried out with these mixed samples. The grinding tests showed that the chemicals used (Na_2SO_4 and KCl) and the grinding time did not have a significant effect on the measurement results. However, this cannot generally exclude the matrix effects during XRF. At this point there is still optimization potential for the development of matrix-adapted standards for the process samples in cement production. The main challenge lies in the composition of the raw meal, as this varies constantly due to the large number of substitute raw materials.

Looking to the future, the cement industry faces further challenges in order to achieve CO_2 neutrality by 2050. One factor is the increase in the use of substitute fuels up to 100 %, which means that the use of fossil fuels is a thing of the past, provided the materials are locally available. For example, the Austrian cement plant in Retznei, operated by “LafargeHolcim”, already uses 100 % alternative fuels.[7]

Furthermore, the proportion of clinker in cement (about 77 % in 2017) can be replaced by alternative materials as additives to a higher extent. However, new alternative materials will have to be used in the future, as the phasing out of coal-fired power plants will limit the substitute raw material fly ash and the use of blast furnace slag will be reduced.[73] Research focuses on the use of calcined clay [74] or silica and pozzolan materials from waste streams.[75][7].

These additives of the future and the further increase in substitute fuels will exacerbate the situation with the entry of undesirable elements, which means that targeted, forward-looking quality planning and control will be essential for a stable process and total compliance. The expansion, refinement, maintenance and use of material flow balances, as developed in this master's thesis for “w&p Zement GmbH”, is an absolute prerequisite for the successful continuation of the cement industry.

Appendix

i. Cement notation and cement types

The cement notation is a simplified form of the chemical formulas. The following abbreviations are used [54]:

C = CaO
M = MgO
S = SiO_2
A = Al_2O_3
F = Fe_2O_3
N = Na_2O
K = K_2O
H = H_2O
s = SO_3

The clinker phases and other important cement compounds can thus be designated as shown in *table 0.1*.

Table 0.1: Notation an nomenclature of major cement compounds. [76]

CHEMICAL NAME	CHEMICAL FORMULA	OXIDE FORMULA	CEMENT NOTATION	MINERAL NAME
TRICALCIUM SILICATE	Ca_3SiO_5	$3CaO*SiO_2$	C_3S	ALITE
DICALCIUM SILICATE	Ca_2SiO_4	$2CaO*SiO_2$	C_2S	BELITE
TRICALCIUM ALUMINATE	$Ca_3Al_2O_6$	$3CaO*Al_2O_3$	C_3A	ALUMINATE
TETRACALCIUM ALUMINO FERRITE	Ca_2AlFeO_5	$4CaO*Al_2O_3*Fe_2O_3$	C_4AF	FERRITE
CALCIUM HYDROXIDE	$Ca(OH)_2$	$CaO*H_2O$	CH	PORTLANDITE
CALCIUM SULFATE DIHYDRATE	$CaSO_4*2H_2O$	$CaO*SO_3*2H_2O$	CsH_2	GYPSUM
CALCIUM OXIDE	CaO	CaO	C	LIME

Table 0.2: Cement types and their composition according to DIN EN 197-1 [wt-%] [77]

Main Cement Types	Normal cement types		Composition of the main ingredients Mass proportions [%] based on the sum of the main and secondary components										Minor Ingrediens
			Portland cement clinker	**Slag sand** S	**Silica dust** (< 10 %) D	**Puzzolans**		**Fly ash**		**Burned slate** T	**Limestone**		
						naturally P	naturally tempered Q	Silica-rich V	lime-poor W		L	LL	
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
	Portland silica dust cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	0-5
	Portland pozzolan cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21-35	-	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II B-Q	65-79	-	-	-	21-35	-	-	-	-	-	0-5
	Portland fly ash cement	CEM II/ A-V	80-94	-	-	-	-	6-20	-	-	-	-	0-5
		CEM II/ B-V	65-79	-	-	-	-	21-35	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	0-5
	Portland slate cement	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	-	0-5
	Portland limestone cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	21-35	0-5
	Portland composite cement *	CEM II/A-M	80-94	12-20									0-5
		CEM II/B-M	65-79	21-35									0-5
CEM III	Blast furnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolan cement *	CEM IV/A	65-89	-	11-35					-	-	-	0-5
		CEM IV/B	45-64	-	36-55					-	-	-	0-5
CEM V	Composite cement *	CEM V/A	40-64	18-30	-	18-30			-	-	-	-	0-5
		CEM V/B	20-38	31-50	-	31-49			-	-	-	-	0-5

* In the Portland composite cements CEM II/A-M and CEM II/B-M, in the pozzolana cements CEM IV/A and CEM IV/B as well as in the composite cements CEM V/A and CEM V/B, the main components apart from Portland cement clinker must be indicated by the name of the cement. [26]

ii. Average chemistry of the analysed input materials

Table 0.3: Average chemistry of the input material for clinker production.

MATERIAL	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cl
LIMESTONE	0.0	0.3	0.5	1.5	0.0	0.1	0.0	55.0	-	-	0.3	0.0
GREY LIME	0.1	0.9	2.9	10.6	0.1	0.1	0.6	54.0	-	-	1.3	0.0
MARL	0.2	1.3	4.9	16.2	0.1	0.1	1.1	46.1	-	-	2.5	0.0
FINE ORE	0.3	3.9	5.0	23.2	0.1	0.7	0.5	11.6	0.3	0.8	47.2	0.0
QUARTZITE	0.1	0.5	4.2	89.5	0.1	0.1	1.9	1.4	0.1	0.0	1.2	0.6
MILL SCALE	0.0	0.2	0.6	1.6	0.1	0.1	0.1	0.6	0.0	1.1	94.4	0.0
RUST ASH	0.8	4.9	8.0	35.5	1.2	0.7	7.8	20.7	0.8	0.4	3.2	0.1
RUST ASH	1.0	3.4	10.0	42.6	1.3	0.7	3.8	16.1	0.6	0.4	3.9	0.1
RUST ASH	1.3	3.7	7.3	38.2	2.1	2.2	4.9	24.1	1.0	1.2	12.2	0.8
RUST ASH	1.8	3.9	7.9	49.5	0.7	1.2	2.1	16.2	1.6	0.3	3.6	0.5
SODA ASH	1.3	1.5	13.2	26.4	0.1	5.1	0.9	27.5	0.5	0.1	4.7	0.0
FLY ASH	0.9	3.4	8.8	30.8	3.7	3.6	4.2	31.6	0.6	1.3	4.4	0.2
FLY ASH	0.2	1.4	11.1	17.3	0.5	0.4	0.4	54.5	0.3	0.5	0.0	0.1
BOTTOM ASH	0.6	2.6	4.1	66.3	1.3	1.6	2.1	13.4	0.2	0.4	1.7	0.0
C-LIME DUST	0.0	33.1	0.8	2.2	0.1	0.7	0.0	22.6	0.0	0.2	0.6	0.1
DRILLING MUD	1.2	3.7	9.5	33.9	0.1	0.7	1.6	24.3	0.3	0.1	2.6	0.0
GREEN LIQUOR SLUDGE	1.7	0.7	0.4	0.6	0.1	2.1	0.4	50.9	0.0	0.4	0.2	0.1
RVA	0.5	11.4	4.7	26.1	1.7	0.0	1.8	43.5	0.3	0.5	2.8	0.1
CONSTRUCTION WASTE	1.1	3.7	9.3	50.2	0.1	0.6	1.3	15.2	0.4	0.1	3.4	0.0
COAL	0.50	-	17.5	33.1	-	5.1	1.2	14.2	-	-	19.4	0.0
PLASTICS	2.20	-	15.6	45.6	-	0.1	1.2	23.4	-	-	3.92	1.3
SEWAGE SLUDGE	0.20	-	17.9	29.7	-	1.1	1.6	18.9	-	-	10.0	0.5

iii. Calculation steps for the chemical concentration of K_2O, Cl, Na_2O and SO_3 of the mixed samples

To calculate the concentrations of K_2O, Cl, Na_2O and SO_3 of the individual mixed samples, the externally or wet-chemically determined K_2O, Na_2O, Cl and SO_3 contents of the reference samples of limestone, marl, raw meal, hot meal, clinker and bypass dust were used as a basis.

For the varying concentrations, different amounts of KCl and Na_2SO_4 were added to a fixed amount of reference sample. For example, different amounts of chemicals were added to 500 g of the reference of clinker, as can be seen from *table 0.4.*

Table 0.4: shows the weight, weights of the chemicals added and the calculated chemical concentration of K_2O, Cl, Na_2O and SO_3 for the blind and mixed samples of clinker

CLINKER

SAMPLE	WEIGHT [G]	KCL_ADD [G]	K_2O [%]	CL [%]	NA_2SO_4_ADD [G]	NA_2O [%]	SO_3 [%]
KLI BP	500.00	0.00	0.83	0.04	0.00	0.38	0.61
KLI P1	502.34	1.31	0.99	0.16	1.03	0.47	0.72
KLI P2	505.83	2.50	1.13	0.27	3.33	0.66	0.97
KLI P3	509.30	3.68	1.27	0.38	5.62	0.85	1.22
KLI P4	513.18	5.27	1.46	0.53	7.91	1.04	1.46

The calculation steps for obtaining the concentrations that were carried out are shown using the KLI P1 example:

Calculation of the K_2O content in the reference sample:

$$K_2O_{BP}[g] = \frac{K_2O\ _{BP}[\%] * m_{BP}\ [g]}{100} = \frac{0.83 * 500\ g}{100} = 4.15\ g$$

Calculation of the K content in the reference sample:

$$K_{BP}[g] = \frac{K_2O\ _{BP}[g]}{MW_{K2O}} * (2 * MW_K) = \frac{4.15\ g}{94.20\ g/mol} * (2 * 39.10\ g/mol) = 3.45\ g$$

Calculation of the K content in the added amount of KCl:

$$K_{KCl\ added}[g] = \frac{KCl_{added}[g]}{MW_{KCl}} * MW_K = \frac{1.31\ g}{74.55\ g/mol} * 39.10\ g/mol = 0.69\ g$$

Calculation of the total K content of the mixed sample:

$$K_{MS}[g] = K_{BP}\ [g] + K_{KCl\ added}\ [g] = 3.45\ g + 0.69\ g = 4.14\ g$$

Calculation of the total K_2O content in the mixed sample:

$$K_2O_{MS}[g] = \frac{K_{MS}\ [g]}{MW_K} * \frac{MW_{K2O}}{2} = \frac{4.15\ g}{39.10\ g/mol} * \frac{94.20\ g/mol}{2} = 5.00\ g$$

Calculation of the concentration of K_2O in the mixed sample:

$$K_2O_{MS}[\%] = \frac{K_2O\ _{MS}[g]\ *\ 100}{m_{MS}\ [g]} = \frac{5.00\ g\ *\ 100}{502.34\ g} = 0.99\%$$

The same steps were carried out to calculate the Cl, Na_2O and SO_3 concentration in the mixed sample.

iv. Calculation steps for the development of the material balance

The analysis results of the chemical composition and heavy metals determined by means of XRF of the input materials and process samples are entered in registers in the Excel sheet. From this the mean value and the standard deviation of the individual elements or heavy metals are calculated using the following equation:

Mean value: $\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$

Standard deviation: $\sigma_x = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n} (x_i - \bar{x})^2}$

The mean values are transferred to the respective registers (raw materials, substitute raw materials, fuels) as links.

Calculation of fuel chemistry and 'KLI + BPS chemistry of fuel' input:

To calculate the fuel chemistry from the analysed average chemistry of the fuels coal, plastic and sewage sludge, a recipe is required which can be entered by the operator in the overview of the mass balance after use. This recipe is used to calculate what percentage of the respective oxides or chlorides are present in the fuel chemistry, as shown in the following *table 0.5* with Na_2O as an example.

Table 0.5: Na_2O-content of the fuels and the used recipe for the calculation of the fuel chemistry.

FUELS	Na_2O [%]	RECIPE FUELS [%]
Coal	0.50	13.39
Plastics	2.20	70.87
Sewage Sludge	0.20	15.75
Chemistry of fuels	**1.66**	-

$$Na_2O_{Fuels}[\%] = \left(Na_2O_{coal}[\%] * \frac{m_{coal}[\%]}{100}\right) + \left(Na_2O_{plastic}[\%] * \frac{m_{plastic}[\%]}{100}\right) + \left(Na_2O_{sewage\ s.}[\%] * \frac{m_{sewage\ s.}[\%]}{100}\right)$$

$$Na_2O_{Fuels}[\%] = \left(0.50\ \% * \frac{13.39\ \%}{100}\right) + \left(2.20\ \% * \frac{70.87\ \%}{100}\right) + \left(0.20\ \% * \frac{15.75\ \%}{100}\right) = 1.66\ \%$$

m … Percentage of the recipe

For the entry of chemicals from the fuels into the clinker+bypass dust material flow, the recipe-fuels must be weighted with the total loss (L) (or ash content), as only a lower mass fraction of the fuel remains after the combustion process. The weighting was carried out with the following equation:

$$m_{coal\_w}[\%] = m_{coal} * \left(\frac{100 - L_{coal}}{100}\right)$$

$$m_{coal\_w}[\%] = 13.39\ \% - \left(\frac{100 - 95.00\ \%}{100}\right) = 0.67\ \%$$

The weighted recipe must then be standardized to 100 % with the following equation to achieve the recipe used to calculate the 'clinker+bypass dust from fuels' chemistry, shown in *table 0.6*.

$$m_{coal\_KLI+BPS}[\%] = \frac{m_{coal\_w}[\%]}{m_{sum\_w}[\%]} * 100 = \frac{0.67\ \%}{25.65\ \%} * 100\ \% = 2.61\ \%$$

Table 0.6 shows the fuels recipe, the recipe weighted and the recipe of 'clinker + bypass dust from the fuels' material flow.

FUELS	RECIPE FUELS [%]	RECIPE_WEIGHTED [%]	RECIPE KLI + BPS [%]
Coal	13.39	0.67	2.61
Plastics	70.87	14.74	57.48
Swedge Sludge	15.75	10.24	39.91
Sum	**100**	**25.65**	**100**

The calculation of the percentage of oxides in the ‘clinker+bypass dust form fuels’ material flow is carried out in the same way as for the fuel chemistry, but for the calculation the clinker+bypass dust recipe is used.

Calculation of the raw meal chemistry and ‘KLI + BPS chemistry of raw meal’ input:

A raw meal recipe is used to calculate the raw meal chemistry, whereby the substitute raw materials used can be selected in the overview and their percentage of raw meal can be entered. The proportion of the remaining raw materials is calculated using the solver, so that the desired secondary conditions are met. The recipe is linked to the raw meal calculation register. Before the raw meal chemistry is calculated using the same scheme as for fuel chemistry (see above), the raw meal recipe had to be converted into the dry raw meal recipe using following equation and after that standardized to 100 %, using the same equation as for the fuel recipe.

$$m_{limestone\_dry}[\%] = m_{limestone} * \left(\frac{100\ \% - Humidity_{limestone}}{100\ \%}\right)$$

$$m_{limestone\_dry}[\%] = 30\ \% * \left(\frac{100\ \% - 2.19\ \%}{100\ \%}\right) = 29.36\ \%$$

For the entry of chemicals from the raw meal into the clinker+bypass dust material flow, the raw meal recipe must be weighted with the loss on ignition (LOI) and then standardized again to 100 %. Calculation is the same as for the recipe weighting of fuel. In this case, the analysed oxides or chlorides of the raw materials and substitute raw materials must also be calculated without ignition loss, which was carried out using the following equation using the example of Na_2O:

$$Na_2O_{\mathrm{RM\_W}}[\%] = Na_2O_{\mathrm{RM}}[\%] + \frac{Na_2O_{\mathrm{RM}}[\%] * \ \mathrm{LOI}\ [\%]}{100}$$

$$Na_2O_{\mathrm{RM\_W}}[\%] = 0.01 + \frac{0.01 * \ 43.00}{100} = 0.02\ \%$$

The further calculations to maintain the chemical composition in the ‘KLI + BPS from raw meal’ material flow are carried out in the same way as for the fuel chemistry calculation, whereby the recipe clinker and the oxides or chloride were used. To check the composition, the LSF, SR and AR are calculated according to *equations 2.1, 2.2 and 2.3*.

Calculation of the total KLI + BPS chemistry:

To get the total KLI+BPS chemistry, the ‘KLI+BPS of raw meal’ and ‘KLI+BPS of fuel’ chemistry must be added in the ratio of the amount of raw meal and fuel used. To do this, the residues of the raw meal or fuel flows must first be calculated after the combustion process by weighting the raw meal or fuel recipe with the ignition loss or total loss, adding and then subtracting from the 100 %. To illustrate this, this is carried out using the example of fuels:

$$Loss_{Fuels}[\%] = \left(m_{Coal}[\%] * \frac{Loss_{Coal}[\%]}{100}\right) + \left(m_{Plastic}[\%] * \frac{Loss_{Plastic}[\%]}{100}\right) + \left(m_{Sewage\ s.}[\%] * \frac{Loss_{Sewage\ s.}[\%]}{100}\right)$$

$$Loss_{Fuels}[\%] = \left(13.39\ \% * \frac{95.00\ \%}{100}\right) + \left(70.87\ \% * \frac{79.20\ \%}{100}\right) + \left(15.75\ \% * \frac{35.00\ \%}{100}\right) = 74.4\ \%$$

$$Residue_{Fuels}[\%] = 100\ \% - Loss_{Fuels}[\%]$$

$$Residue_{Fuels}[\%] = 100\ \% - 74.4\ \% = 25.6\ \%$$

The residue from raw meal is 63.8 % and from fuel 25.6 %.

With the calculated residues, the input of raw meal and fuel used can be converted to the output after the burning process.

$$Output[t/h] = \frac{Input\ [t/h] * Residue\ [\%]}{100}$$

$$Output_{RM}[t/h] = \frac{140\ t/h * 63.8\ \%}{100} = 89.3$$

$$Output_{Fuels}[t/h] = \frac{15.5\ t/h * 25.6\ \%}{100} = 4.0$$

Thus, the output of raw meal and fuel result in an output of the KLI+BPS material flow of 93.3 t/h, which was calculated as follows.

$$Output_{KLI+BPS}[t/h] = Output_{RM}[t/h] + Output_{Fuels}[t/h]$$

With the calculated outputs of raw meal and fuel, the raw meal and fuel ratio can be calculated.

$$Ratio_{RM} = \frac{Output_{RM}}{Output_{RM} + Output_{Fuels}}$$

$$Ratio_{Fuels} = \frac{Output_{Fuels}}{Output_{RM} + Output_{Fuels}}$$

This results in a raw meal ratio of 0.96 and a fuel ratio of 0.04.

The total KLI+BPS chemistry is obtained by adding of KLI+BPS of raw meal and fuel chemistry in the ratio, as explained using the example of Na_2O:

$$Na_2O_{KLI+BPS}[\%] = Na_2O_{KLI+BPS_{RM}}[\%] * Ratio_{RM} + Na_2O_{KLI+BPS_{Fuels}}[\%] * Ratio_{Fuels}$$

$$Na_2O_{KLI+BPS}[\%] = 0.15\ \% * 0.96 + 1.36\ \% * 0.04 = 0.20\ \%$$

Calculation of the clinker chemistry:

To calculate the clinker chemistry, the outputs of clinker+bypass dust, bypass dust and clinker were required. For this purpose, the respective outputs of clinker and bypass dust were calculated using a bypass dust rate, which can be entered in the overview, based on the total output of KLI+BPS:

$$Output_{KLI}[t/h] = Output_{KLI+BPS} - \frac{Output_{KLI+BPS} * BPS\,rate}{100}$$

$$Output_{BPS}[t/h] = Output_{KLI+BPS}\,[t/h] - Output_{KLI}\,[t/h]$$

This resulted in an output of 92.64 t/h for clinker and 0.65 t/h for bypass dust.

With the respective outputs of KLI+BPS and bypass dust, the individual output of the oxides or chloride of the KLI+BPS material flow and of the BPS material flow could be calculated. For this, the bypass dust chemistry was entered in the overview. The calculation is explained using the example of Na_2O for the output of BPS:

$$Na_2O_{BPS_{Out}}[t/h] = \frac{Na_2O_{BPS}[\%] * Output_{BPS}[t/h]}{\sum Oxides\,[\%]}$$

$$Na_2O_{BPS_{Out}}[t/h] = \frac{1.49\,\% * 0.65\,t/h}{94.48\,\%} = 0.01\,t/h$$

To obtain the output of clinker oxides, the individual output of oxides from bypass dust flow are subtracted from the output of oxides from KLI+BPS flow, as shown here using the example of Na_2O:

$$Na_2O_{KLI_{Out}}[t/h] = Na_2O_{KLI+BPS_{Out}}[t/h] - Na_2O_{BPS_{Out}}[t/h]$$

$$Na_2O_{KLI_{Out}}[t/h] = 0.20\,t/h - 0.01\,t/h = 0.19\,t/h$$

The clinker chemistry can then be calculated using the output of clinker.

$$Na_2O_{KLI}[\%] = \frac{Na_2O_{KLI_{Out}}[t/h]}{Output_{KLI}[t/h]} * 100$$

$$Na_2O_{KLI}[\%] = \frac{0.19\,t/h}{92.64\,t/h} * 100 = 0.20\,\%$$

To check the composition, the LSF, SR and AR are calculated according to *equations 2.1, 2.2* and *2.3.*

The calculation of the heavy metals is carried out analogously to the calculation of chemistry.

Calculation of heavy metal content in cement:

In order to calculate the heavy metal content in cement, the recipe-cement is required, which can be entered in the overview register.

This recipe is used to calculate how high the proportion of the respective heavy metals is in the finished cement. The calculation is shown using the example of Ca, seen in *table 0.7.*

Table 0.7 shows the recipe for cement and the Ca-content of the materials used.

MATERIAL	RECIPE_CEMENT [%]	Ca-CONTENT [ppm]
CLINKER	75	787847
GYPSUM NATURAL	2	530510
GYPSUM REA	3	549102
SLAG SAND 2	8	456298
SLAG SAND 1	7	386719
FLY ASH	2	38671
LIMESTONE	3	1233331

$$Ca_{Cement}[ppm] = \left(Ca_{clinker}[ppm] * \frac{m_{clinker}[\%]}{100}\right) + \left(Ca_{gyp\_N}[ppm] * \frac{m_{gyp\_N}[\%]}{100}\right) + \ldots + \left(Ca_{limestone}[ppm] * \frac{m_{limestone}[\%]}{100}\right)$$

$$Ca_{Cement} = \left(787847ppm * \frac{75\ \%}{100}\right) + \left(530510\ ppm * \frac{2\ \%}{100}\right) + \ldots + \left(1233331ppm * \frac{3\ \%}{100}\right) = 719316\ ppm$$

v. Figures of the calibrations of raw stone, raw meal, hot meal, clinker and bypass dust

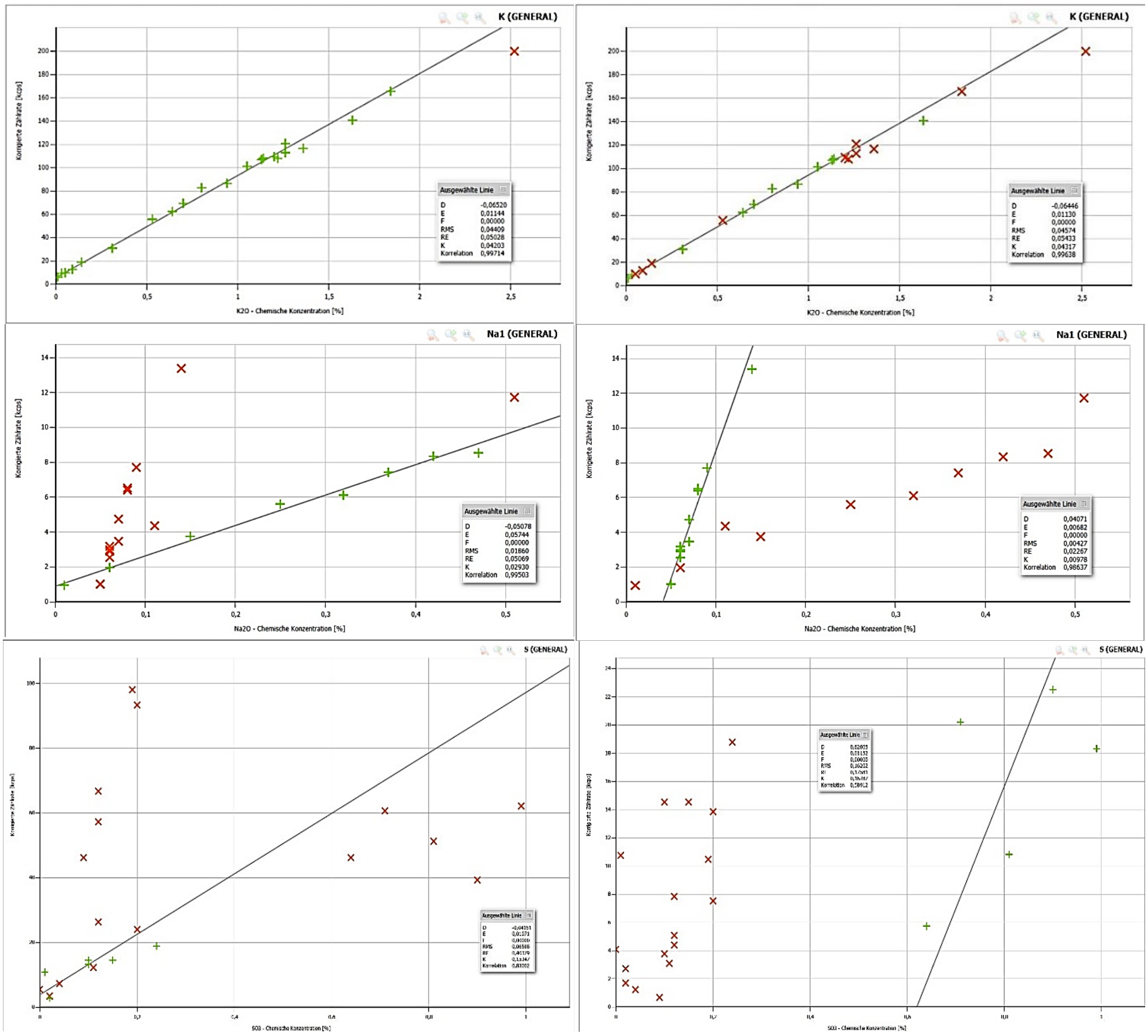


Figure 0.1 shows the calibration lines of raw stone for potassium, sodium and sulphur. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side.

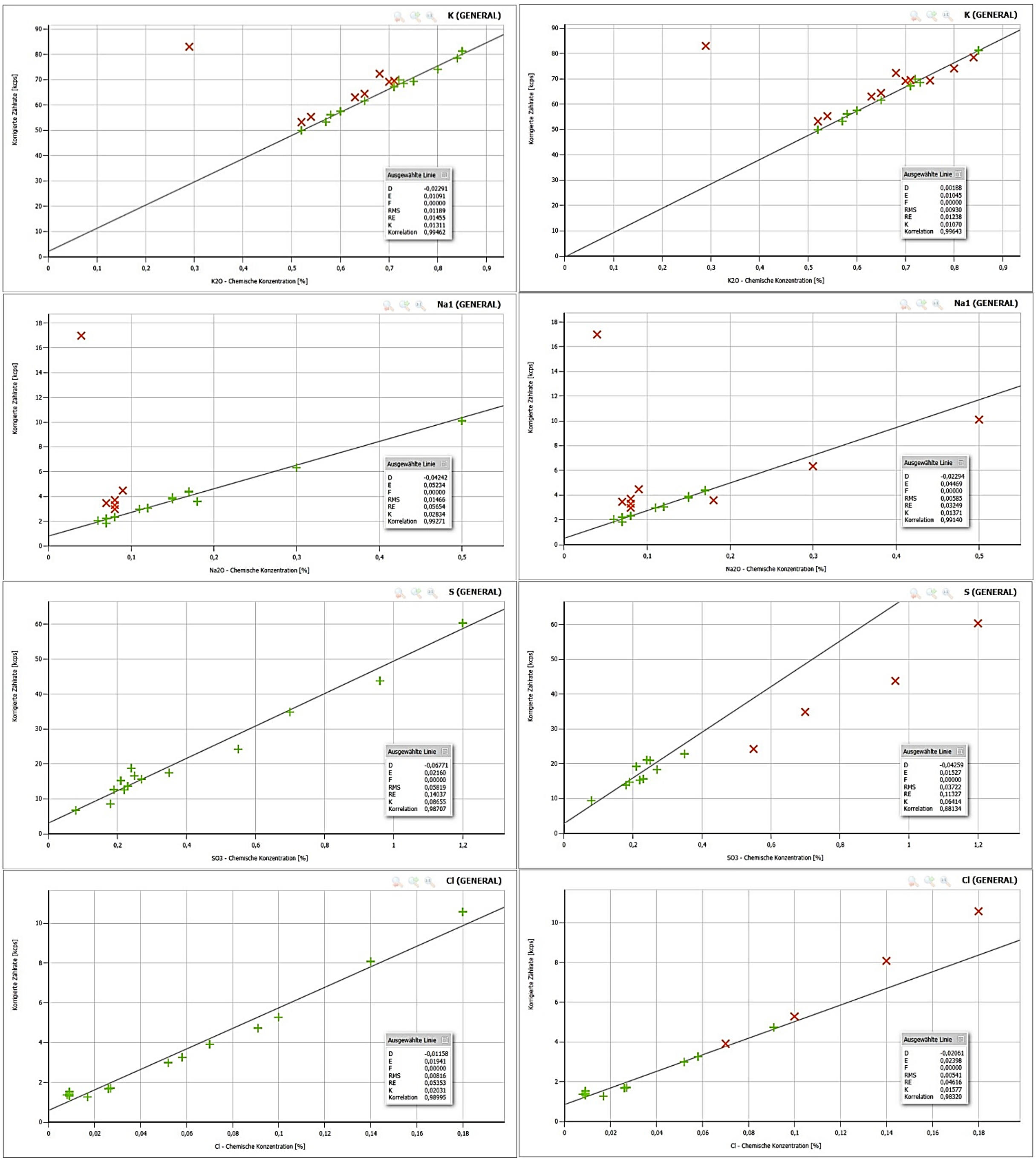


Figure 0.2 shows the calibration lines of raw meal for potassium, sodium, sulphur and chloride. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side.

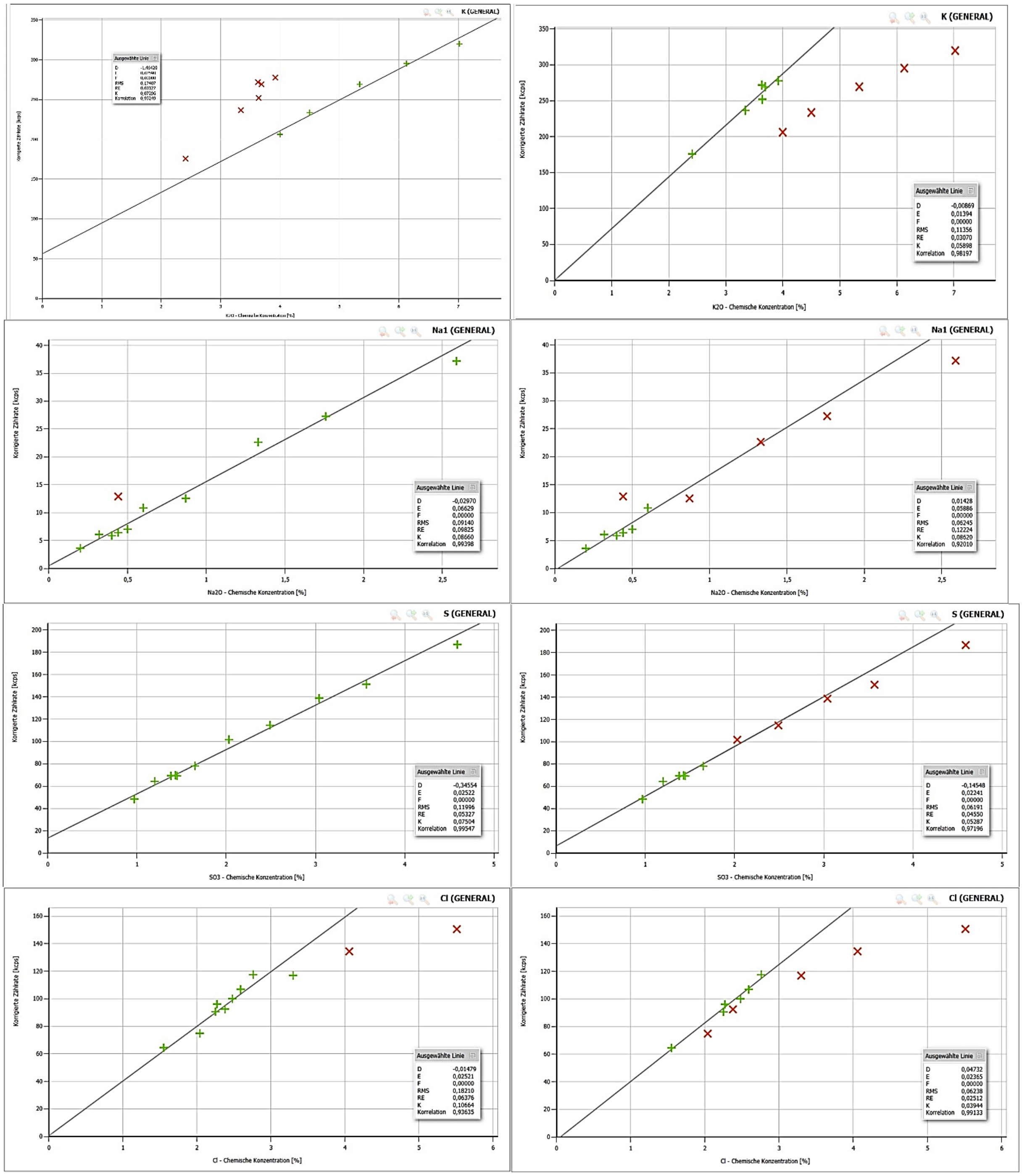


Figure 0.3 shows the calibration lines of hot meal for potassium, sodium, sulphur and chloride. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side.

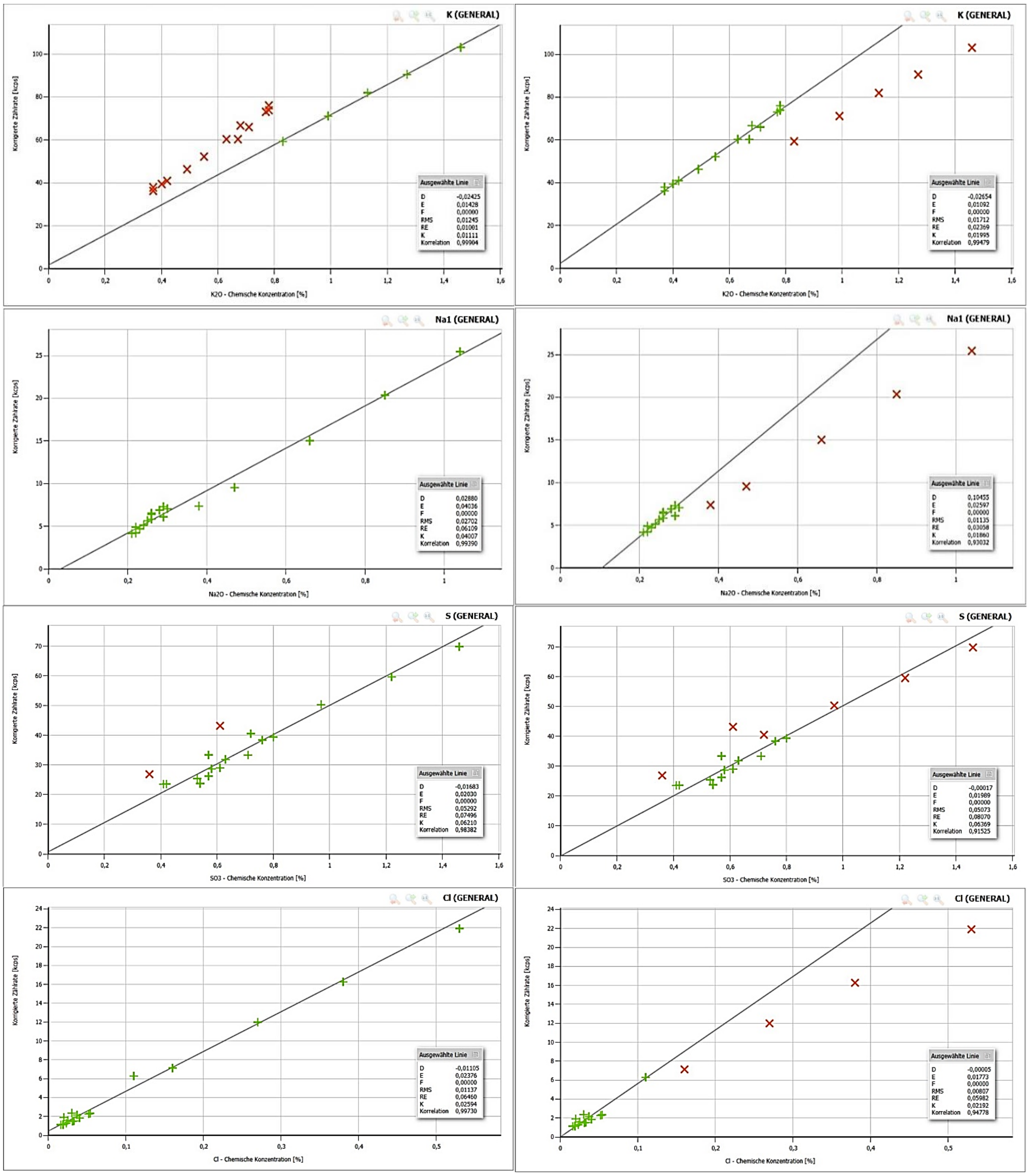


Figure 0.4 shows the calibration lines of clinker for potassium, sodium, sulphur and chloride. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side.

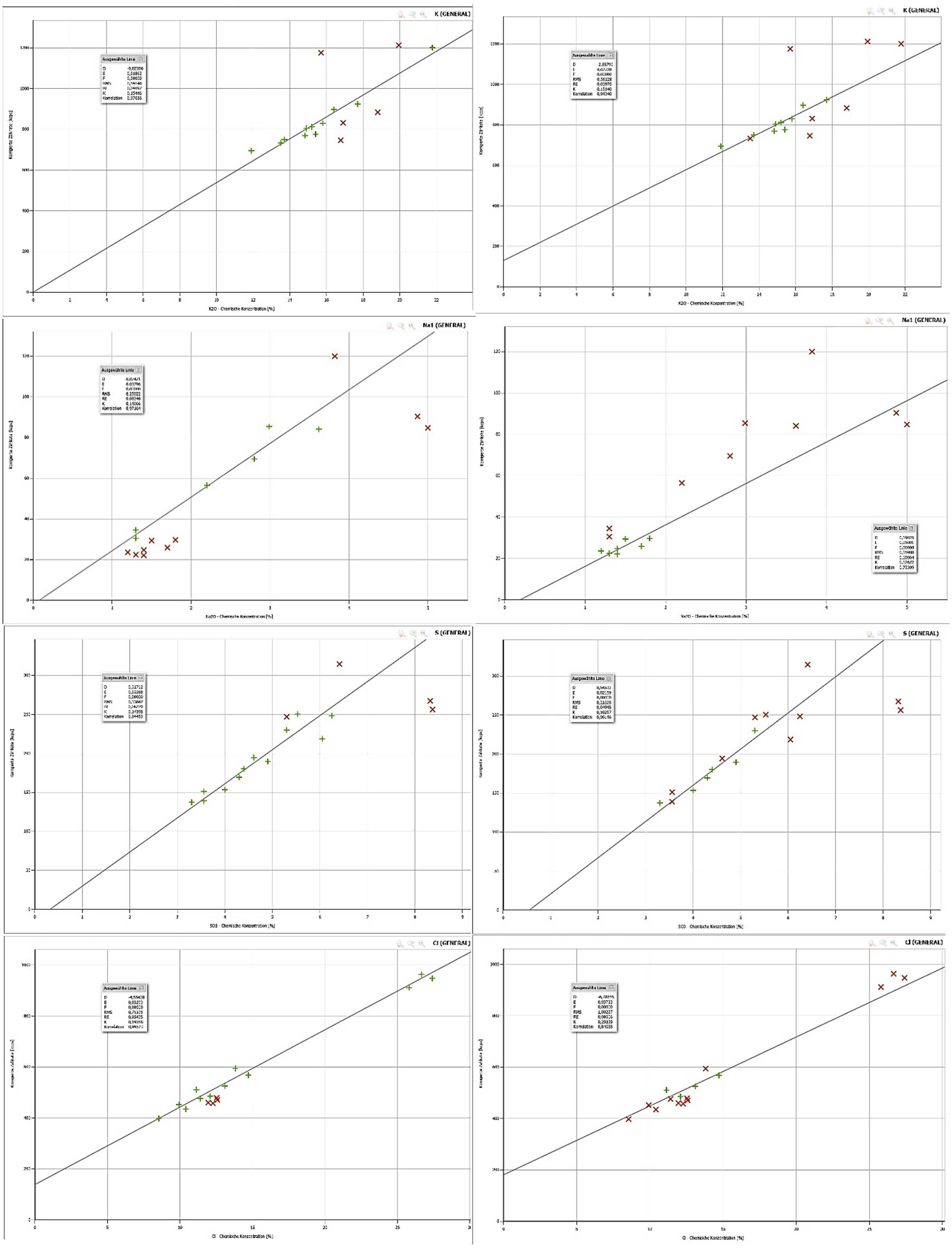


Figure 0.5 shows the calibration lines of bypass dust for potassium, sodium, sulphur and chloride. The new calibration lines establish with the mixed samples is shown on the left and those with the historical standards on the right side.

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