CHARACTERIZATION AND QUALITY CONTROL OF CLAY RAW MATERIALS AND CERAMIC BATCHES FROM THE RAW MATERIAL SUPPLIERS POINT OF VIEW

by Fiebiger, W; Heuser, W; Althof, J; Titz, B

Stephan Schmidt KG
Bahnhofstraβe, 92
Dornburg, 2
GERMANY

1. INTRODUCTION

Supply possibilities of quality-proof raw materials in accordance to production and product requirements are essential for the modern ceramic industries on the one side; on the other side they are marketing and sales arguments for raw material producers. They claim to do their best to guarantee quality - ISO 9000, European and national standards, quality assurance systems and certificates are key issues in sales negotiations, where they are used with more or less justification. Proportionally, the raw material consumer is more or less satisfied with the products.

From the suppliers point of view the production of functional raw materials for specific applications becomes problematic - each industrial sector, each client has its individual quality parameters with regard to fabrication techniques and product characteristics; consequently, there are no such things as **the** sanitaryware batch, **the** tiles clay, **the** vitrified clay pipe formulation.

Things are even more complicated, as quality control systems and methods are usually not identical on both sides. Finally, one has to bear in mind that the raw material producer has to be the servant of several masters, without always having, however, the detailed expertise of the highly specialized client.

A very decisive criteria is the feasibility of quality control in terms of costs and time. With all respect to norms and standards - hardly anybody is willing to accept additional costs to this regard.

It is the objective of this contribution to discuss quality control requirements under the aspect of efficiency from the raw material producers point of view, and to describe the function of verticalized control systems - without neglecting the limitations of such methods.

2. DEFINITION

Systems and methods of raw material production and preparation have been comprehensively discussed and published in literature.

Summarizing, the following definition shall be given:

"Winning and processing of ceramic raw materials and batches comprise all the necessary steps and measures to transform technically non-functional natural raw material components of more or less homogeneous compositions into functional standardized blends in a defined processing stage according to pre-established quality parameters.

Raw material parameters, production and product related ceramic characteristics have to be controlled and maintained during all production steps."

In other words, one raw material or a group of raw materials of unspecified technical characteristics have to be transformed into a functional product according to customer specification.

The control of certain parameters in different preparation steps is required, since a number of ceramic raw materials show a "non-linear" behaviour in blends, meaning that ceramically relevant parameters may not always be prognosticated mathematically on the basis of data evidence form single components.

As an example we shall refer to green modulus of rupture measurements in two single clays. Both indicate a comparatively low M.O.R.

A sequence of test blends, surprisingly, shows "non-linear" results; in the specific case, the M.O.R. is clearly higher than the theoretical arithmetical mean value - and not directly prognosticable.

It has to be concluded that for quality control purposes not only laboratory data have to be gathered; they also have to be interpreted; - it also may be assumed that by means of statistical data treatment characteristics of blend systems can be prognosticated on the basis of single raw material data, provided sufficient statistical evidence is available.

Based upon the above consideration the following methodology may be defined.

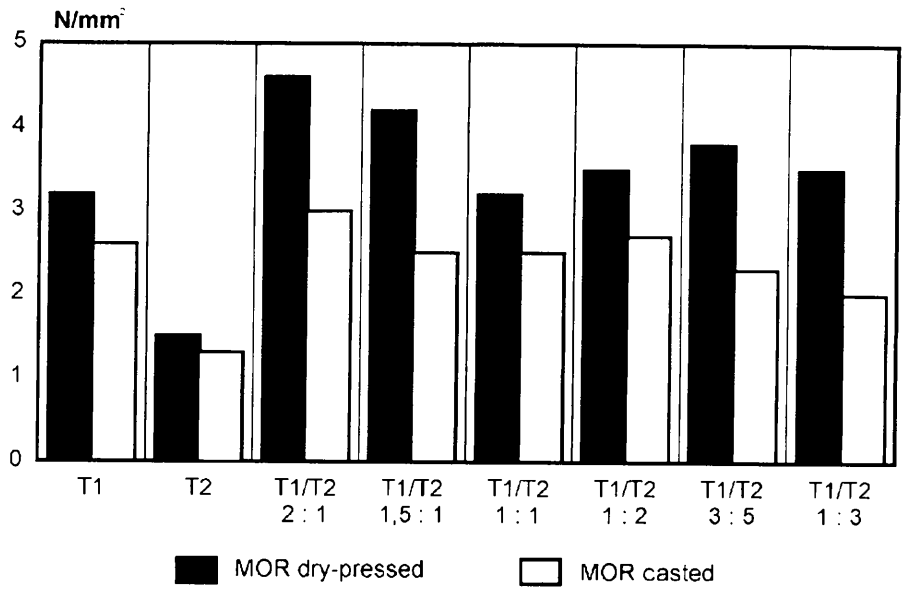
2.1 RAW MATERIAL DATA ASSEMBLING

Single raw materials are to be tested with regard to their fundamental ceramic characteristics; lab data have to be suitable for subsequent computer based data treatment.

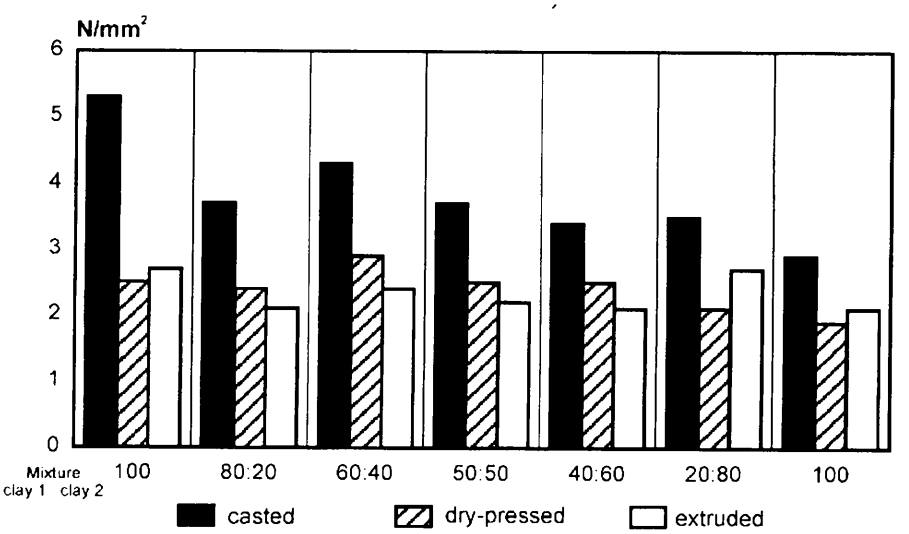
Typical parameters are:

- shrinkage
- loss on ignition
- water absorption
- chemical composition
- firing colour
- grain-size distribution
- residue

GREEN MODULUS OF RUPTURE



GREEN MODULUS OF RUPTURE IN CLAY MIXTURES



A modern ceramic laboratory is able to realize these examinations in acceptable ranges of time and costs.

Additional investigations are necessary to establish

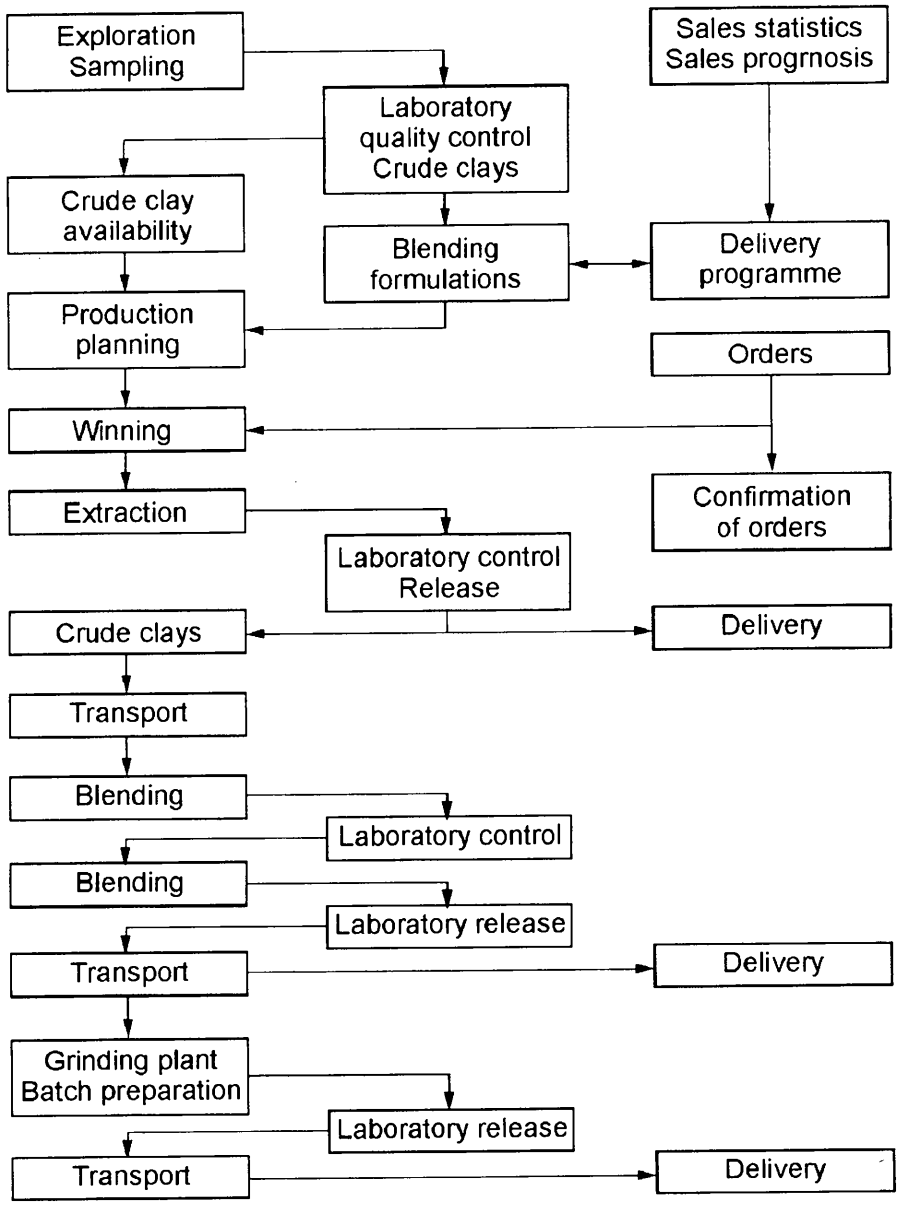
- modulus of rupture
- mineralogical composition
- rheological parameters
- coefficients of dilatation

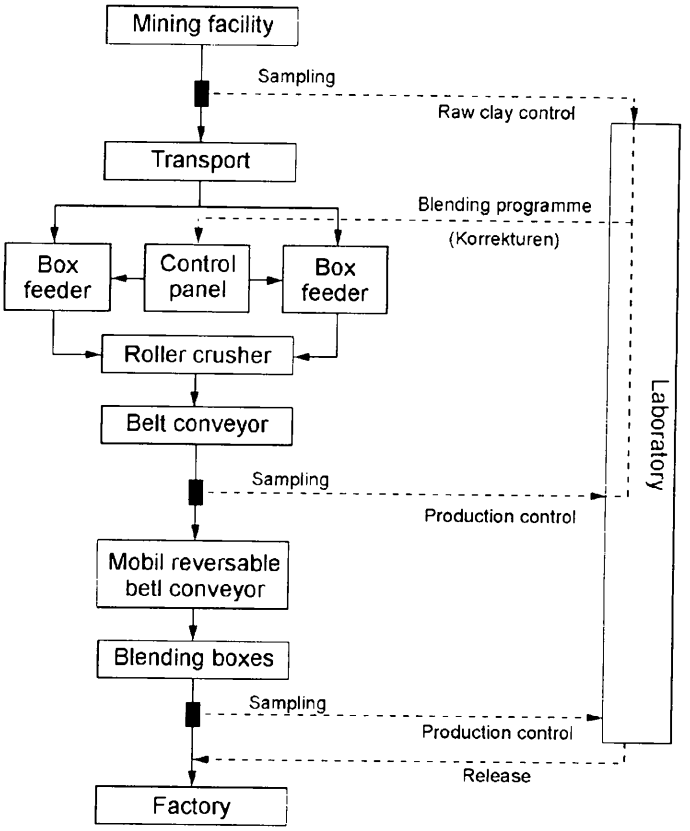
Which require substantially more time, and are usually not suitable as control parameters during production. For the definition of new concepts and the development of new products, however, they are indispensable.

2.2 ELABORATION OF BASIS DATA FOR PRODUCTION PLANNING

The general flowsheet for raw material production and preparation indicates the fundamental influence of quality characterization and control on the overall process.

Considering the potential large number of single raw materials in different mining sites and storage areas it becomes evident that customer- and product-orientated production principally depends upon the availability of the correct components at the right moment. The optimal utilisation of winning, transport capacities and storage capacities (boxes, silos, etc.) is only possible if raw material parameters are available before production starts. "Just in time" production, consequently, does not apply only to contract delivery deadlines, but especially to the production readiness at different points in the flowsheet. In accordance to this postulation the raw material parameters have to be available just in time.





As a rule of thumb the following planning steps may be defined:

- strategic planning (> 2 years) on the basis of exploration results
- operational planning (> 6 months) on the basis of drilling and trenching results
- production planning
  (≥ 4 weeks in general)
  (≤ 1 week real time planning)

on the basis of channel and production samples

With increasingly detailed planning the production is strictly sales orientated. Consequently,

- planned standard (= blended clays) product quantities are used to calculate the requirements for crude clay components to be extracted from the winning facilities.

- as a general rule winning is executed in a way that all single components are available "just in time" - in the pits or in storage areas.

2.3. PRODUCTION MANAGEMENT

Besides winning and transportation parameters the production management requires the examination of characteristics of standard clay qualities to be produced.

A standard formulation has to be established for each product quality, which is to be followed in blending the defined single components. Consequently, the components are laboratory controlled before the blending process starts, the composition of the final standard product is prognosticated for a given quantity and the result is controlled again.

Once again it has to be stressed that ceramic parameters are not always to be defined as a linear function of percentual blending formulas. Without any problem the chemical composition of a blend can be calculated on the analysis of the single components and consequently - at least to a certain extent - the firing colour, as an example. The task becomes more complex when different single component parameters may influence the characteristics of the blend.

As an example, the interaction of grain-size distribution, specific grain surface, and mineralogical composition may define the modulus of rupture in extremely different ways. This may also apply with regard to rheology, firing behaviour, eutectic conditions, etc.

3. GENERAL CONSIDERATIONS

Based upon the a.m. definitions one basic concept is relevant:

The characterization of ceramic raw materials is realized in two steps:

1. Conceptional

- Identification of raw material parameters in a general sense (physical and chemical) and with regard to ceramic production and product criteria. Based upon classification results standardized products and blending concepts are developed in accordance to technological requirements of respective markets.

Standards for each product are established.

2. Operational

- control of established quality parameters and standards
- correction according to laboratory control data before and during production
- final product control

Consideration with regard to operational aspects such as capacities, analytical methods, staff qualifications will be elaborated later.

Some basic criteria, however, have to be discussed at this point.

3.1 RAW MATERIALS

Mineral raw materials show natural variations deriving from specific conditions at the stage of origin. This relates principally to chemical and mineralogical composition but also to physical parameters such as grain size distribution and specific grain surface, which are quality-relevant in ceramic industries.

Contrary to the production of several other mineral raw materials the fabrication of plastic ceramic raw materials, e.g. clays, does not interfere with the original composition by enrichment or reduction of certain components (which is technically possible but economically not feasible).

The production techniques principally aim to homogenize the - partly extremely complex - multi-mineral mixes to introduce defined products into controllable blending processes.

The basic principle is defined as follows:

"Only specified, homogenized and controlled single raw materials may be transformed into defined standard blends.

The fact that natural raw materials show discontinuous variation results in a more or less significant tolerance of each production lot from the standard. These deviations have to be identified accordingly."

To realize this representative sampling is required.

3.2 SAMPLING SYSTEMS

According to the respective planning levels and production steps samples for the characterization of the raw materials have to be taken systematically. The quality of information regarding the analyzed parameters is a function of frequency and density of samples and the sampling technique.

In a first step drilling of exploration holes is executed and the cores are analyzed and correlated. According to the drilling grid or borehole distances the results reveal a more or less representative information on the contents of a deposit. Usually these results are not sufficient to classify the quantities and qualities in terms of winning parameters. For short term production planning additional channel samples at the different mine faces are required. The results give detailed information with regard to the composition of a production lot. Even this sample gives only a two-dimensional information on a complex three-dimensional volume.

Is the automatic sampling of a continuous production stream more accurate, where a defined quantity yields defined sub-quantities under constant and controllable conditions. By subsequent blending and quartering a representative production sample is recovered, which represents the characteristics of a production lot. The laboratory results are basis for the blending formulation and quality control during and after subsequent production steps.

The concept also requires the homogenization of each sub-quantity in a mixing bed in order to minimize or eliminate deviations during blending.

Experience shows that automatic sampling systems in continuous production streams are substantially more representative if compared to samples taken from trucks or railway waggons.

At this point aspects of costs and time required must not be neglected. The importance of "correct" sampling is reflected in numerous investigations and standards (e.g. ISO 8656).

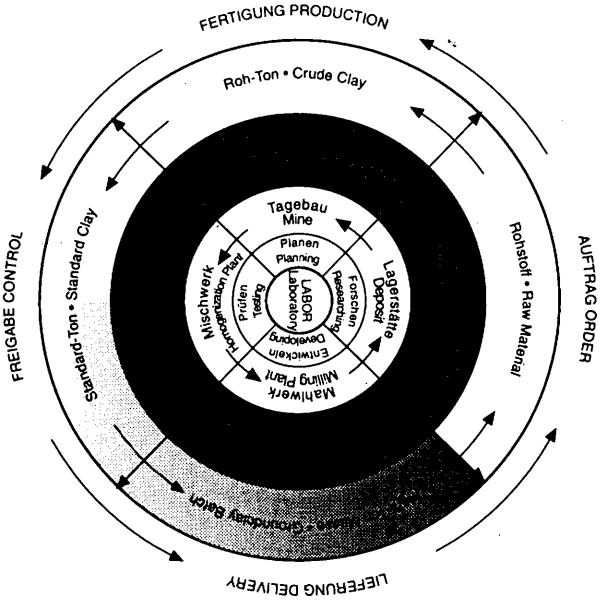
4. INTERNAL STANDARDS FOR QUALITY CONTROL

While we have been basically discussing methods aimed to characterize raw materials with regard to data collection and production control the following shall focus on laboratory techniques and methods.

Fundamental principles for quality control

- the control system and each working step have to be standardized
- each measurement or test has to be repeatable at any time
- each laboratory result has to be reproducible at any time
- each result has to be comparable to other results at any time

- each sample for testing purposes has to be reproducible at any time
- each laboratory result has to make reference to the preparation and testing method applied.



These parameters are of fundamental importance for statistical data treatment. On the other hand, it is essential to maintain cost and time efforts at an economic level. Considering that today up to 15% of the total direct operational costs derive from laboratory control work, it becomes evident that the limits for standard ceramic batch components are reached and little is left for additional control steps.

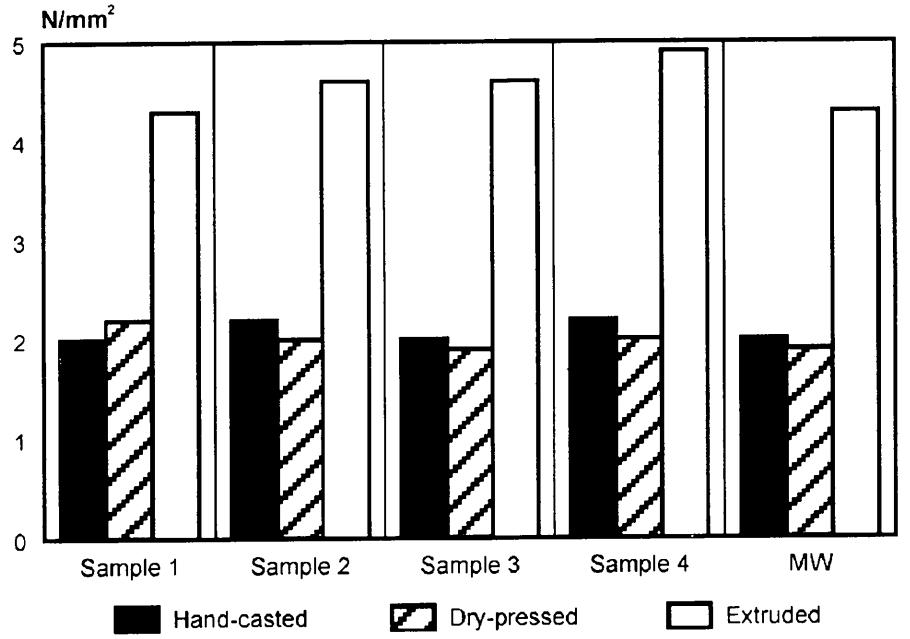
The modern laboratory technique offers a large range of most variate equipment for each test. There are almost no limitations to prices; qualities of results and equipment handling, however, do not always correspond to the price labels. One also has to bear in mind that different methods may yield different results, which are system-related; grain size analysis is a typical example.

As far as the preparation of samples is concerned, different methods may result in confusing data. If we take the preparation of test specimens for the determination of the green modulus of rupture we find out that the same sample yields completely different results.

It is essential that results are always reproducible with regard to internal standards and comparable with other testing methods. Continuous calibration of equipment and external control measurements using other systems are required to build up conversion charts - if possible.

In anticipation to the quality documentation for the customer chapter it is pointed out that laboratory data sheets should always make reference to analytical methods and sample preparation techniques.

GREEN MODULUS OF RUPTURE



TEST PROCEDURE

First, the sample material is crushed and dried. Then it is ground in a blade disintegrator and, finally, dry pressed (hydraulic compacting pressure:- 300 bar) to obtain round specimens. After residual drying, colorimetry, weighing and measuring in preparation for determination of loss on ignition and firing shrinkage, two each specimens are heated to 1170°C in 120 minutes in electric-heated laboratory-type fast-firing kilns. The fired specimens are then examined with regard to their CIE-Lab tristimulus values, fired colour, loss on ignition, firing shrinkage, water absorption and chemical composition. The same specimens are used for determining the coefficient of expansion. The routine testing scope provides for determination of water absorption in a vacuum chamber by extracting the air out of the open pores and replacing it with water.

PARTICLE-SIZE TESTING WITH A SEDIGRAPH 5100

In parallel with the other ceramic examinations, a SediGraph 5100 measures the grain-size distribution of each dry, preground sample. An automatic sampling station enables continuous testing. The particle size range of interest is 0.5 - 100 μm. Both in quantity and in quality, the results correspond closely to those of conventional sedimentation analysis, e.g. after Andreasen. The measuring principle of the SediGraph 5100 is based on sedimentation. The particles are dispersed - with water normally being used for clay - and then pumped into a sample cell. The concentration of the particles is scanned by an X.ray beam. The intensity of the transmitted X-ray beam serves as a measure of the concentration of mass at a certain point in time at a certain position within the cell.

CHEMICAL ANALYSIS

The use of energy-dispersive X-ray fluorescence systems for the analysis of chemical elements dates back to 1966. In such a system, the secondary radiation passes directly from the sample into the detector. The detector - an Si(Li) barrier-layer type - measures the energy of the material-specific X-ray quanta. The source of excitation is a low-power X-ray tube that operates between roughly 5 and 50 kV and 0,01 to 1 mA. The programmed analysis time is 200 seconds. The absorbed energy is

readied for evaluation by a multi-channel analyzer with a monitor for spectral characterisation. The diagram shown on the monitor is a test-analogous I(E)-histogram [I(E) = intensity as a function of energy]. A computer calculates the quality of the individual elements.

COLORIMETRY

The sample material is illuminated by a standard illuminant. A Xenon lamp producing close to standard light D is used for the measurement, i.e. for flashing the standardized test plate with the standard light. The surface tint registered by the photometer is characteristic of the spectral reflection values.

The values determined are correlated with the three spatial axes. The L*,a*,b* system developed by Judd Hunter (standardized in 1976: DIN 6174, CIE-Lab 1976) represents the location of the light-dark axis (L* value), the location of the red-green axis (a* value) and the location of the blue-yellow axis (b* value). The advantage of the L*, a*, b* system is that mathematically identical distances in all colour zones yield exactly the same distances in the graphic system.

The complete laboratory procedure of each sample, analytical and testing steps and parameters, consequently, have to be executed and controlled according to the lab standard and documented.

5. EVALUATION OF LABORATORY DATA

Analytical and testing data as indicated above are compiled in the electronic data bank.

The immediate confrontation with single component and/or batch standards on the screen shows possible deviations of single data related to the respective production lot and makes corrections possible which incidentally could be calculated and proposed by the computer.

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GV...:  7.2 *  7,6 *  8,0      7,600    S63.0: xx.x * xx.x * xx.x       99,400
WA...:  5,9 *  6,9 *  7,9      6.500    S40,0: xx.x * xx.x * xx.x       97.100
SiO2.: 67.5 * 69.0 * 70.5     68.820    S20.0: xx.x * xx.x * xx.x       95,300
TiO2.:  1.5 *  1,6 *  1,7      1.590    S10,0: xx.x * xx.x * xx.x       90,200
Al2O3: 24.7 * 26.0 * 27.3     23.080    S 6,0: xx.x * xx.x * xx.x       85.200
Fe2O3:  0.9 *  1,0 *  1,1      1,320    S 2,0: xx.x * xx.x * xx.x       72.800
CaO..:  0,1 *  0.2 *  0.3      0,000    S 1,0: xx.x * xx.x * xx.x       64.000
MgO..:  0,3 *  0.4 *  0,5      0.000    S 0.5: xx.x * xx.x * xx.x       53.900
K2O..:  2.0 *  2,1 *  2.2      2.150    Feinabs...40 my:  xxxxxxx        0,000
Na2O.:  0.1 *  0.2 *  0.3      0,000    Feinabs...63 my:  max.1,0        3,100
Brennfarbe: creme                003    Feinabs..200 my:  xxxxxxx        0.000
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Using statistical methods the data quality and plausibility may be controlled. The use of a larger data basis makes the prognostication of batch parameters by means of regressive analysis possible; reference is made especially to non-linear parameters as discussed above.

The quality and reliability of these methods is a direct function of the accuracy of measurements of the quantity of data available.

6. DATA SHEETS

Quality parameters on the basis of laboratory evidence are the commanding elements for the production of standardized blends and batches. In addition, there is the quality proof for the customer at delivery time. It has to be observed, however, that following the preceding considerations each production lot shows slight deviations with regard to the idealized standards.

The acceptable tolerances are established in the production standard data sheets, and products are cleared by the quality management only when all laboratory control data are within the pre-established (or sometimes with the customer arranged) ranges.

Raw material data sheets in sales catalogues usually contain general information and must not be confused with production data sheets.

The data quality derives from long term statistical evaluation and is a representative mean value, which - by principle - is not suitable for production planning and quality control; they do not refer to specific production requirements.

RAW MATERIAL DATA SHEET

1302
S263

Chemical analysis, calcined

SiO_2	71,5%
TiO_2	1,6%
Al_2O_3	22,5%
Fe_2O_3	1,0%
MgO	0,5%
CaO	0,2%
K_2O	2,0%
Na_2O	0,2%

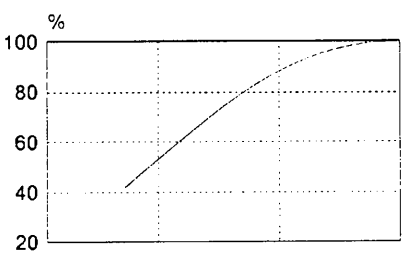
Mineral composition

Kaolinite group	44%
Mica group	18%
Montmorillonite group	-%
Quartz	32%
Others	<7%

Loss on ignition		6,3%
Sieve residue	>63 µm	<2,5%
Dry bending strength		4,3 N/mm²
Drying shrinkage		3,8%
Deflocculation	>320° Gal. $Na_2O \cdot SiO_2$	3,5%

Particle size distribution

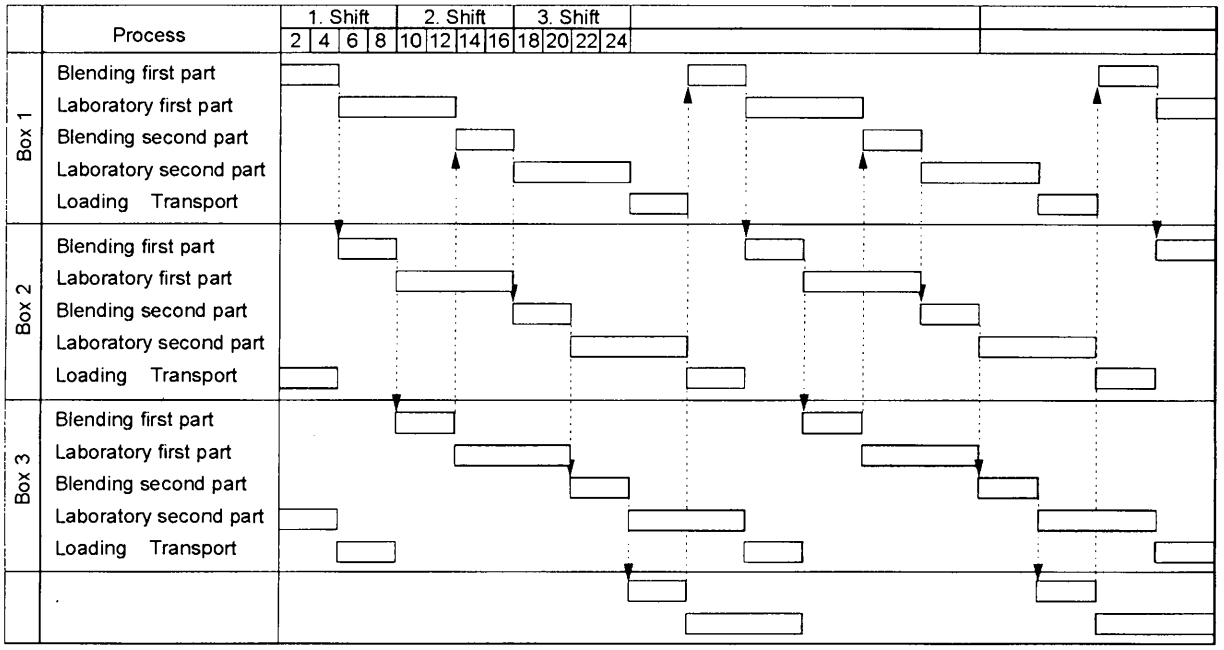
< 63 µm	99,1%
< 40 µm	98,5%
< 20 µm	96,4%
< 10 µm	91,3%
< 6 µm	83,7%
< 2 µm	63,2%



7. CAPACITY CONSIDERATIONS

The characterization of clay raw materials - as an instrument to manage production planning, production and quality - depends on the laboratory equipment and flowsheet, analytical methods and laboratory staff qualifications from the capacity point of view. In addition, winning, transport and storage capacities have to be considered as well as costs.

One of the principle objectives of these investigations is to reduce the overall production cycles for single lots.



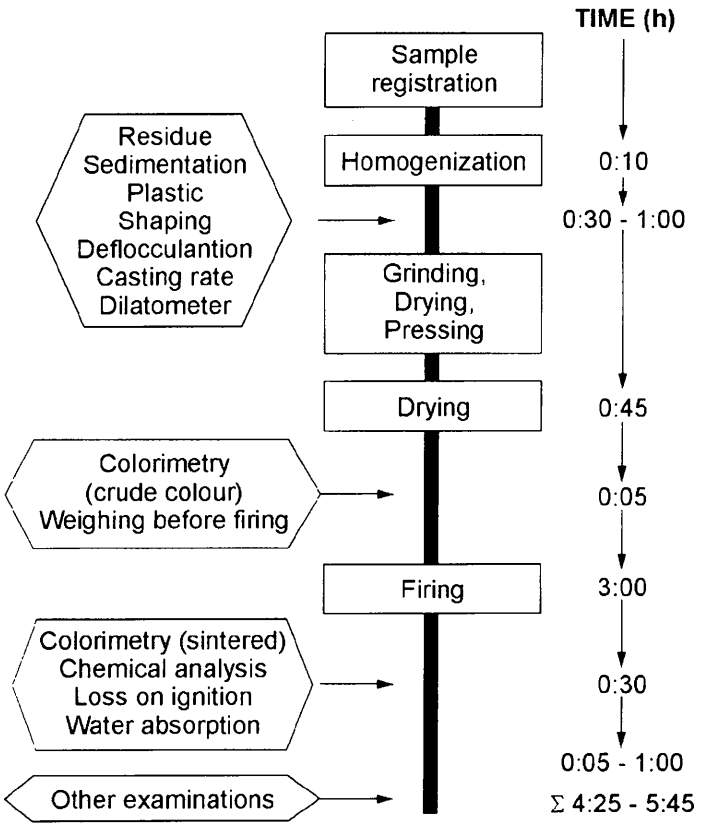
Consequently, all samples being taken before production starts may be analyzed and tested in great detail without critical limitations in the time available. The methodology of sampling at that stage, however, results in a relatively low grade of reliability, that is to be improved during production. The reduction of testing steps per sample to accelerate the production control is limited by the fact that certain results and parameters cannot be prognosticated on the basis of preceding parameters. Control measurements have to be considered accordingly.

In a general sense, the objective is to optimize the use of capacity by reduction of laboratory control steps during production.

Capacity bottle necks may result from unscheduled variations in total number of samples due to modifications in production programmes or corrections in batch formulations due to lab control results.

The synchronization of production and quality systems is an extremely useful exercise for all persons involved and may lead to substantial cost reductions.

This applies also to erroneous laboratory results which automatically add costs. As a rule of thumb, a modern ceramic laboratory has to be equipped to the extent of being able to establish and control standard ceramic parameters within one work shift.



Applying the usual industrial standards and norms, however, would automatically result in substantially longer laboratory working times and would increase the cost per sample.

8. THE SUPPLIER-CUSTOMER CONNECTION

As stipulated initially, the objective of winning and preparation of ceramic raw materials is the production of custom-tailored production-adapted blends, which technological parameters are guaranteed by quality control systems. Consequently, the production is realized and controlled according to customer specifications..

The definition of relevant quality parameters to be tested and the respective methodology have to be agreed upon following the considerations with regard to deviations due to different test methods. At least, test results have to be made comparable by parallel control measurements ("round robin"). In specific cases additional laboratory tests have to be agreed upon and costs have to be considered.

In practical terms, quality agreements have to make reference to parameters, which are of priority to the specific type of raw material; such as modulus of rupture, firing behaviour, colour, etc.

It has to be remembered that even optimized standard products are following the natural limitations of the single components. One has to compromise with regard to secondary parameters in order to obtain reliable quality for the important criteria. There is no such thing as a perfect ceramic raw material.

It is, however, possible to produce mixes and blends adapted to the specific production requirements, provided that laboratory data are reproducible under production conditions.

9. STANDARDISATION OF TEST METHODS AND DATA

Test methods are integral parts of raw material data as discussed previously.

The application of standardized unified test methods would be highly desirable. We recognize that this is obviously a utopical position, since the objectives of quality control are of fundamental difference if we compare laboratories of raw material producers and consumers. Thus, the realization of parallel tests to make results comparable is something to compromise.

In particular, preparatory steps such as grinding, milling, drying and deriving effects on test results must not be neglected.

As far as mathematical-statistical systems of data treatment are applied, relevant information has to be established and exchanged.

Especially these methods are considered to be of growing importance for raw material characterization, since it may be assumed that the total laboratory work with regard to single analytical steps per sample may be reduced by applying such methods. The use of directly established raw material parameters to prognosticate production and production-relevant characteristics is in many cases the state of the art.

It goes without saying that a close cooperation of the suppliers and customers laboratories is required for the development of such quality control systems. The part-time exchange of laboratory staff is a successful tool to improve methods and communications.

10. CONCLUSIONS AND RECOMMENDATIONS

To conclude it can be stated that one laboratory result is only of relative significance. It requires explanations especially regarding its origin - test equipment, methodology - and regarding its quality - reliability, reproducibility.

A certain number of independent test results contains direct and indirect information on parameters of the tested raw material.

The interaction of single parameters and its significance for ceramic behaviour may be calculated and prognosticated by means of mathematical and statistical methods.

According to our experience there is a highly attractive potential of research and development in this field - not only for raw material suppliers and ceramic industries but especially for research institutions and universities.

It is worthwhile to discuss together with those institutions how new , quick and reliable test methods could be developed, which would respond to the ever growing requirements of the ceramic industry and the suppliers of ceramic raw material and batch suppliers.