W. Russ, N. Schmid, R. Meyer-Pittroff

Heat treatment of kieselguhr in order to improve filtration properties and for recycling

The heat treatment for the recycling of used kieselguhr from deep bed filtration at 500 °C for 120 minutes in the presence of water vapor improves the filtration properties of the recycled kieselguhr. The cumulative increase in pressure across the filter bed of the pilot filter as a parameter for the maximum duration of filtration rose more gradually over time. The total amount of filtration time increases, therefore reducing filter down time. The turbidity, as a measure of filtration precision, does not increase. The water value and the permeability both increase with heat treatment. The particle size distribution indicates that structural changes were uncommon as a result of heat treatment. The specific surface area and the pore volume of the kieselguhr was reduced one third and the pore surface area, by 70 %. Additionally, the average pore diameter was almost doubled. The more decrease in filtration pressure, together with the higher values for turbidity both resulted from a change in pore size and a reduction in the adsorptive characteristics of the particles due to the heating process. Heat treatment presumably caused a reduction in smaller pores. Only the larger pores remained open, which lowered the resistance of the filter bed, increasing the flow rate through it. As a consequence, the filter bed compressed more slowly, which resulted in a more gradual pressure increase during filtration. Measuring the flow and the zeta potential, the amount of specific charge all prove that the adsorptive properties of the particles were reduced because of their diminished surface area and their reduction in surface area charge.

BC 08 Process technology/ 24 Bottling/ 79 Other by-products

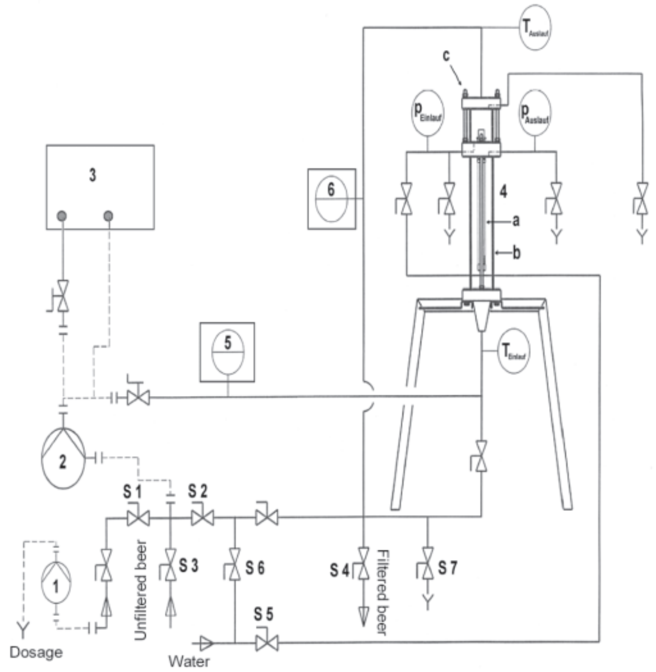
(Descriptors: Filtration, kieselguhr, recycling.

Deskriptoren: Filtration, Kieselgur, Recycling).

1 Kieselghur sludge recycling – state of the art and goals

The current means by which kieselguhr from the brewing industry is recycled in Germany is through heat treatment. Presently, there is only one plant in operation which can recycle kieselguhr in this manner. This is done by first combining used kieselguhr obtained from various breweries, and then removing a portion of the water mechanically. Afterwards, the kieselguhr is dried before being sent to a high temperature mixing chamber, where it is heated to temperatures between 700 and 780 °C using forced air. This kieselguhr can only be added at the rate of 50 % of the total kieselguhr needed for in-line dosing during filtration (1, 2). There are also other kieselguhr recycling methods available and still more are in development; however, none have seen practical application (3, 4, 5).

WTU Wärmetechnik und Umweltschutz GmbH in Jena, the König Brauerei in Duisburg and the Chair for Energy and Environmental Technologies of the Food Industry of the Technischen Universität München have worked in cooperation to develop a new recycling method for used kieselguhr from breweries based on heat treatment. This method consists of a preliminary drying step followed by heat treatment achieved through hot gas in counter flow where a maximum temperature of 500 °C is reached. During the entire process, steam is present in the hot gas. The



1 Dosing pump (ProMinent® Model gamma G/4 1203)
2 Beer pump (Heidolph GmbH Model PD 5230 with pump head ZP 3)
3 In-line cooling system (Cornelius GmbH Model Eurtotex 100)
4 Candle filter (KHS AG custom-made filter)
5 Flow meter (Krohne GmbH Model IFM 6080 K)
6 In-line turbidity meter (SIGRIST Photometer AG Dual Scat model)
S Location of sensors (Ahlborn Mess- u. Regeltechnik GmbH with various sensors)

Fig. 1 Schematic model of the pilot filtration system (8)

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Table 1 Technical specifications of the filter candle (7)

Description	Specifications
Candle diameter	34 mm
Candle length	340 mm
Wire mesh of wedge wire candle	30 µm
Metal filter area	0.033 m^2
Kieselguhr capacity	9 kg/m^2

Table 2 Mass ratios and absolute mass of pre-coating and dosing

	Mass ratios (%)	Mass (absolute)	Filter aids
First pre-coat	40 + 60	600 g/m²	perlite + coarse kieselguhr
Second pre-coat	40 + 60	600 g/m²	coarse kieselguhr + medium fine kieselguhr
Continuous dosage	100	50 g/hl	medium fine kieselguhr

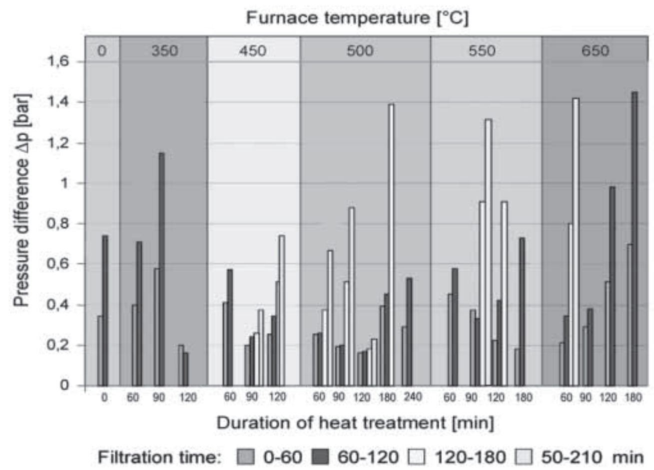

Fig. 2 Pressure difference between filter inlet and outlet over time with respect to the time required to complete filtration with varying temperature and duration of the heat treatment of kieselguhr type A

resulting kieselguhr exhibits distinctly different filtration properties than new kieselguhr. For in-line dosing, it is possible to utilize 100 % kieselguhr recycled exclusively with this kind of heat treatment. Further testing showed that the rise in pressure during filtration was markedly slower than normal. These results indicate that the filtration properties of kieselguhr may be improved through supplemental heat treatment or through heat treatment as part of a recycling procedure (6).

The goals of these experiments were to optimize the parameters time and temperature for the heat treatment of recovered kieselguhr and to document the changes which occurred in its properties.

2 Materials and methods

The experiments were performed at the Bavarian State Brewery Weihenstephan on Helles beer with two different types of kieselguhr, a type A fine to medium fine kieselguhr from France and a type B medium fine from Iceland. The unfiltered beer contained 500,000 yeast cells/ml. Each sample was taken from the lager tank during the brewery's routine filtration.

The filtration experiments were carried out on a pilot filtration system, which is pictured in Figure 1.

The custom-made candle filter is based upon the GETRA ECO candle filter technology from KHS AG. The technical data of the filter candle are summarized in Table 1.

Pre-coat formation and dosing occurs as shown in Table 2.

The following analyses were carried out according to MEBAK (9): water content, change in mass with increased temperature, pH, soluble iron, wet density and water permeability.

Particle size was measured according to the principle of laser diffraction with a Mastersizer from Malvem GmbH. The crystalline portion of the kieselguhr was detected through X-ray diffraction using an X-pert-MPD PW 3040 from Phillips AG. The specific surface area according to Brunauer, Emmett and Teller was determined by means of gas adsorption in accordance with DIN 66131 (10) using a GEMINI 2360 from Micromeritics GmbH. The measurements of the pore size were achieved through gas adsorption with an ASAP 2000 from Micromertitics GmbH. The zeta potential was indirectly determined by measuring the electric potential with a Particle Charge Detector PCD 02 from Mütek Analytic GmbH. A correlation with the zeta potential was able to be demonstrated through parallel measurements of the samples with a Zetasizer. Additionally, the amount of surface area charge present was measured using the PCD 02 from Mütek Analytic GmbH. An acidic polyethensulfonic solution of sodium served as the cationic polyelectrolyte, while poly-dially-dimethyl ammonium chloride solution was utilized as the anionic polyelectrolyte. Differential scanning calorimetry was selected as the thermoanalytical method to be used for these experiments. The purpose of these tests was to document the physical and chemical reactions occurring at higher temperatures, which would indicate changes in the properties of the kieselguhr.

The heat treatment was performed in a muffle furnace model HR 260 from WC Heraeus GmbH. This furnace was modified in order to ensure that water vapor was continuously present in the space where the kieselguhr was fired.

Results for the thermal treatment of the kieselghur and the influence on the beer filtration

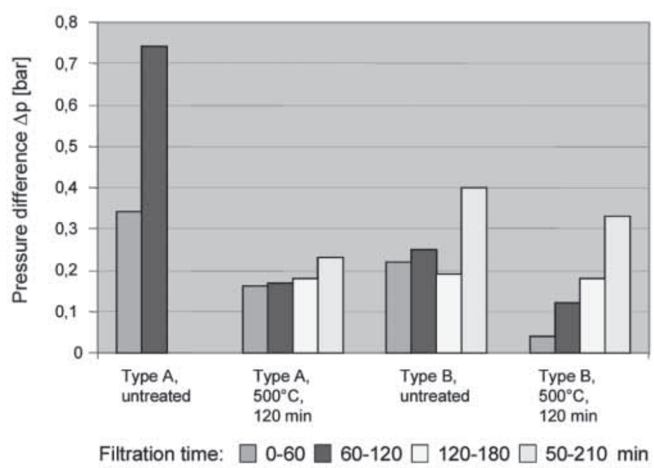

Fig. 3 Pressure difference between filter inlet and outlet over time with respect to the time required to complete filtration varying temperature and duration of the heat treatment

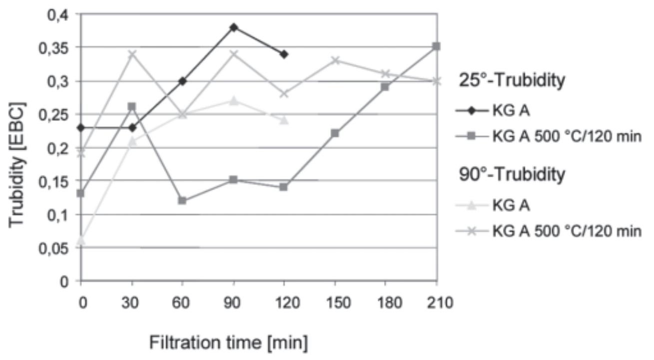

Fig. 4 Values for turbidity of the heat-treated and the untreated type A kieselguhr

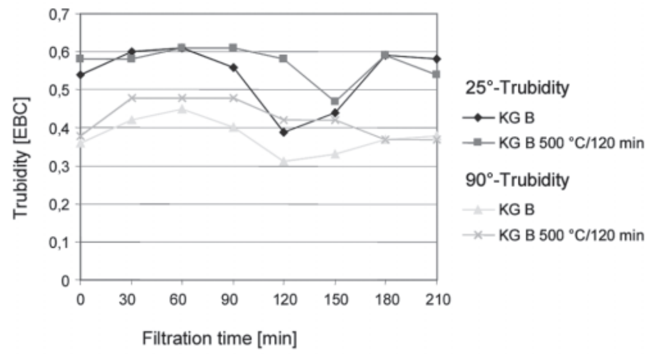

Fig. 5 Values for turbidity of the heat-treated and the untreated type B kieselguhr

Table 3 25° and 90° turbidity (EBC method) of beer filtered with heat-treated type A kieselguhr (mean values over the total filtration time)

Temperature (°C)	–	350	350	350	450	450	450	500	500	500	500	500	550	550	550	550	650	650	650	650
Duration (min)	–	60	90	120	90	120	180	60	90	120	180	240	60	90	120	180	60	90	120	180
Turbidity 25º (EBC)	0.32	0.37	0.31	0.29	0.37	0.28	0.37	0.23	0.47	0.24	0.3	0.13	0.26	0.23	0.4	0.28	0.54	0.54	0.89	0.99
Turbidity 90º (EBC)	0.23	0.37	0.21	0.28	0.46	0.26	0.5	0.28	0.36	0.33	0.36	0.27	0.27	0.26	0.32	0.31	0.59	0.49	0.77	0.99

Table 4 Beer analyses performed on the filtered and unfiltered beer (filtration with kieselguhr type A, heat-treated at 500 °C for 120 min)

	Filtered beer	Unfiltered beer
Original gravity (%)	11.92	11.13
Alcohol content (% vol.)	5.50	5.12
pH	4.47	4.42
Color (EBC)	6.71	5.84
CO_2 (g/l)	4.16	3.35
Apparent gravity (% by mass)	1.56	1.45
True gravity (% by mass)	3.53	3.29
Apparent degree of attenuation (%)	87.00	87.00
True degree of attenuation (%)	70.43	70.43
Bittering units (EBC-BU)	24.5	21.4
Viscosity (mPa*s)	1.68	1.64
Free alpha-amino-nitrogen (mg/l)	115.6	97.5
Polyphenols (mg/l)	272	205
Anthocyanogens (mg/l)	125	106
Diacetyl (mg/l)	0.03	0.03
Pentosan content (mg/l)	0.02	0.02

Table 5 Physical analysis of heat-treated (500 °C for 120 min) and untreated type A kieselguhr

		Untreated	Treated
pH		6.1	6.2
Watervalue	(g/l)	20	22
Permeability	(mDarcy)	108	121
Specific surface area	(m²/g)	7.3	5.2
Specific pore surface area	(m²/g)	5.5	1.7
Specific pore volume	(mm³/g)	22.0	13.0
Mean pore diameter	(nm)	16.0	30.6
Current potential	(mV)	–204	–181
Zeta potential	(mV)	–16.3	–14.5
Specific charge	(µeq/g)	6.2	5.0

Table 6 Comparison of the particle size of type A kieselguhr before and after heat treatment

	d10 (µm)	d50 (µm)	d90 (µm)	d100 (µm)
Untreated	2.42	12.48	48.12	120.67
Treated	2.37	12.31	48.56	123.78

The type A kieselguhr was heat-treated in the furnace described above and subsequently cooled prior to beginning the filtration. Before the kieselguhr was fired, the furnace was preheated to the required temperature.

Figure 2 shows the pressure difference between filter inlet and outlet of the pilot filter. The temperature and duration of heat treatment were varied with respect to the time required to complete the filtration. The rate of pressure increase across the filter bed was lower in each case with the heat-treated kieselguhr than with untreated kieselguhr. The temperature and duration of the heat treatment optimal for a minimal increase in pressure across the filter bed was 500 °C at 120 min.

The increase in pressure during filtration time using the type B kieselguhr was also lower than that of untreated type B. However, as Figure 3 shows, the differences between the two were not as pronounced as with heat-treated and untreated type A.

The values for turbidity (EBC method) of the fine to medium fine type A kieselguhr (Fig. 4), are lower that those for the type B kieselguhr (Fig. 5). The heat treatment at 500 °C for 120 min had no influence on the turbidity values for either type of kieselguhr.

The turbidity is dependent upon the time and the duration of the heat treatment. As seen in Table 3, heat treatment at temperatures over 550 °C yields turbidity values greater than 0.5 EBC, which are unacceptable.

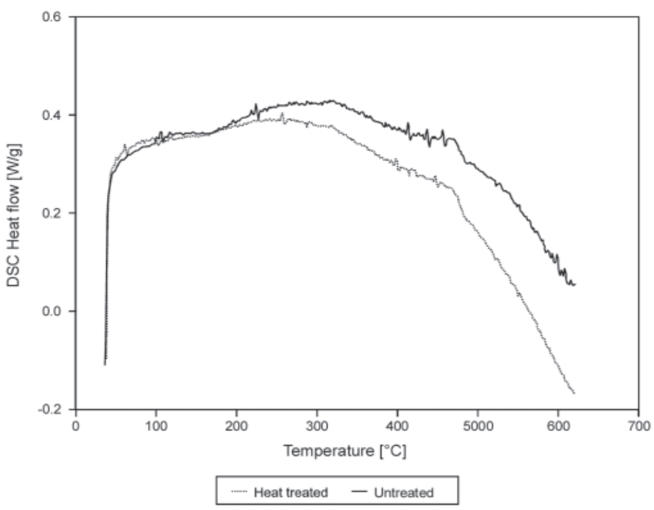

Fig. 6 DSC results for type A kieselguhr, untreated and heat-treated

The beer analyses in Table 4 show that there were no noticeable differences between the beer filtered using the heat-treated and the untreated kieselguhr.

Heat-treated (500 °C for 120 min) and untreated type A kieselguhr were further tested for changes in structure, size and surface area.

The heat-treated sample of the type A kieselguhr exhibited no change in particle size compared to the untreated sample. The average particle diameter of the two differed only slightly; the untreated sample possessed a average particle diameter of 12.5 µm, whereas the mean particle diameter of the heat-treated sample was 12.3 µm. The values for d_{10}, $d_{50,}$ d_{90} and d_{100} for the two samples are given in Table 6.

In Figure 6, the DSC results have been shifted against one another for the sake of clarity. No apparent differences exist between the heat-treated and the untreated samples. The DSC results are very similar.

3 Evaluation and discussion of results

The heat treatment at temperatures no higher than 500 °C for an optimum duration of 120 min in the presence of water vapor improved the filtration properties of the kieselguhr. The cumulative increase in pressure across the filter bed of the pilot filter rose more gradually over time using the heat-treated type A kieselguhr than with the untreated kieselguhr. The use of heat-treated kieselguhr increased the total amount of filtration time possible, therefore reducing filter down time. Given that the heat treatment took place under the optimal conditions described above, the turbidity, as a measure of filtration precision, does not increase in comparison with untreated kieselguhr. The extent to which the filtration properties of heat-treated kieselguhr were able to be improved was also dependent upon the origin and type of kieselguhr.

The water value and the permeability both increase with heat treatment; however, the significantly improved performance of the type A kieselguhr cannot be described solely using these two parameters. The particle size distribution indicates that structural changes were uncommon as a result of heat treatment. Also, sintering processes in the furnace could be excluded at temperatures below 550 °C. The DSC results showed no changes as a result of heat treatment. Neither exothermic nor endothermic reactions took place, nor did a crystalline phase change occur to any extent worth mentioning. The specific surface area of the kieselguhr heated for 120 min at 500 °C was reduced by 29 %, and the pore surface area, by 70 %, as compared to an untreated sample. Additionally, the average pore diameter was almost doubled, from 16 µm to 30 µm. The pore volume of the heat-treated kieselguhr was 29 % smaller than that of the same untreated kieselguhr. The simultaneous decrease in the specific area, increase in the pore diameter and reduction in the pore surface area ultimately lead to the improved filtration properties of the heat-treated kieselguhr. The more gradual increase in filtration pressure, as well as the higher values for turbidity under the influence of temperature both resulted from a change in pore size and a reduction in the adsorptive characteristics of the particles. The adsorptive nature of kieselguhr is directly related to its amount of accessible surface area.

Heat treatment presumably caused a reduction in the smaller pores through sintering, and therefore lessened the possibility for interaction between the kieselguhr and the suspended particles. Thus, more suspended particles were able to pass through the filter bed causing the values for turbidity to increase. Only the larger pores remained open, which lowered the resistance of the filter bed, increasing the flow rate through it. As a consequence, the filter bed compressed more slowly, which resulted in a more gradual pressure increase during filtration. Although the pores experienced a reduction in size through sintering, this only became significant with respect to turbidity when temperatures greater than 650 °C were reached in the muffle furnace. The zeta potential, the amount of specific charge and the electric potential all indicate that the adsorptive properties of the particles were compromised because of their diminished surface area and their change in surface area charge.

The changes observed in the heat treatment of kieselguhr in a modified muffle furnace are essentially identical to those which take place during recycling used kieselguhr with the WTU method. This accounts for the positive changes in the recycled kieselguhr described above. The implications of these results are not only that kieselguhr can be recycled, but that its filtration properties can be improved at the same time.

4 Zusammenfassung / Resumé

Russ, W., Schmid, N., und Meyer-Pittroff, R.: Thermische Behandlung von Kieselguren zur Verbesserung der filtrationstechnischen Eigenschaften und zum Recycling von Kieselgurschlamm — Monatsschrift für Brauwissenschaft 56, Nr. 7/8, 134 – 140, 2003

BC 08 Verfahrenstechnik/ 24 Abfüllung/ 79 Sonstige Nebenprodukte

Die thermische Behandlung von Kieselgurschlamm aus der Tiefenfiltration in Wasserdampfatmosphäre bei 500 °C für 120 min führt neben dem Recycling zu einer Verbesserung der Filtrationseigenschaften der Kieselgur. Die Druckdifferenz zwischen Filtereinlauf- und -auslauf als Parameter für die maximale Filtrationsdauer steigt wesentlich langsamer an. Die Zeit bis zum Abbruch der Filtration und dem damit verbundenen Filterstillstand (Reinigung) verlängert sich. Die Trübung des filtrierten Bieres als Maß für die Filtrationsschärfe nimmt nicht zu. Wasserwert und Permeabilität nehmen zu. Die Korngrößenverteilung zeigt, dass es kaum zu Strukturveränderungen kommt. Die spezifische Oberfläche und das Porenvolumen werden um ca. ein Drittel und die Porenoberfläche um 70 % reduziert, wobei sich der mittlere Porendurchmesser verdoppelt. Für die Erniedrigung der Druckdifferenz durch die Temperatureinwirkung ist die Veränderung der Porengröße und die Reduzierung der für adsorptive Vorgänge zur Verfügung stehenden Oberfläche verantwortlich. Da nur noch größere Poren offen sind, wird dem Flüssigkeitsstrom ein geringer

Widerstand des Filterkuchens entgegengesetzt, d.h. die Kieselgurschicht verdichtet sich langsamer, wodurch die Druckdifferenz langsamer als sonst üblich steigt. Auch die Messungen von Strömungs- und Zetapotential sowie der spez. Ladungsmenge beweisen, dass die Adsorption aufgrund der verringerten Oberfläche und veränderten Oberflächenladung reduziert wird.

Russ, W., Schmid, N., et Meyer-Pittroff, R.: Traitement thermique du kieselguhr pour l'amélioration des propriétés de filtration et pour le recyclage des boues de kieselguhr — Monatsschrift für Brauwissenschaft 56, No. 7/8, 134 – 140, 2003

BC 08 Génie de procédé / 24 Soutirage / 79 Autres produits dérivés

Le traitement thermique des boues en atmosphère de vapeur d'eau à 500 °C pendant 120 min. du kieselguhr en provenance de la filtration en profondeur, conduit à une amélioration des propriétés de filtration du kieselguhr. La différence de pression entre l'entrée et la sortie du filtre, paramètre de la durée maximale de filtration, augmente plus lentement. Le temps jusqu'à la fin de la filtration et la durée d'immobilisation (nettoyage), s'allonge. La turbidité de la bière filtrée, comme mesure de l'efficacité de filtration, n'augmente pas. La valeur d'eau et la perméabilité augmentent. La distribution de la taille des particules montre qu'il n'y a pratiquement pas de variations. La surface spécifique et le volume des pores sont réduits d'un tiers et la surface des pores de 70 %. Le diamètre moyen des pores a doublé. Pour la diminution de la différence de pression sous l'influence de la température, sont responsables : le changement de la taille des pores et la réduction de la surface disponible pour les phénomènes d'adsorption. Bien qu'il n'y ait plus que des grandes pores disponibles, il y a peu de résistance de la part du gâteau de filtration, c'est à dire, la couche de kieselguhr se bouche plus lentement et par conséquent la différence de pression croît plus lentement que d'habitude. Les mesures des flux et du potentiel zéta, ainsi que les charges spécifiques prouvent également que l'adsorption basée sur une diminution de la surface et le changement de la charge de surface sont réduits.

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Manuskripteingang 08. 04. 2003

Buchbesprechung

Prozessleittechnik für die Verfahrensindustrie

Eine verfahrenstechnische Anlage in der Prozessindustrie wird ebenso wie eine Anlage zur Behandlung fester Abfälle in der Abfallwirtschaft von Verfahrensingenieuren geplant und deren Betrieb von Ingenieuren der Prozessleittechnik gewährleistet. Dabei war und ist es bis heute immer wieder von neuem schwierig, eine durchgängige Wissensdisziplinen übergreifende Planung zwischen der Verfahrens- und Prozessleittechnik ohne Missverständnisse durchzuführen, so dass sich auch heute noch immer eine Schnittstelle zwischen der Verfahrens- und Prozessleittechnik zeigt, die es zu beseitigen gilt.

War bisher der Fokus einer verfahrenstechnischen Anlage die Produktion bestimmter Produkte, rückt die Anlage heute in den gesamten Geschäftsprozess vom Einkauf der Rohstoffe bis zum Verkauf der Produkte. Durch diese Integration und die Entwicklungen heutiger Informationstechnologien getrieben, öffnet sich die technische Welt zunehmend der kaufmännischen Welt eines Unternehmens. Zum horizontalen kommt der vertikale Austausch von Informationen hinzu, so dass neue, von betriebswirtschaftlichem Wissen geprägte Informationen, die an bestehendes Wissen wiederum anzukoppeln sind, hinzukommen. Dies erzeugt eine weitere zu beschreibende Schnittstelle zwischen der technischen und kaufmännischen Welt.

Dieses Buch soll die beiden Schnittstellen zwischen der Verfahrens- und Prozessleittechnik sowie zwischen der Prozess1eittechnik und Betriebswirtschaft aufzeigen, um mit dem Aufkommen der zweiten Schnittstelle auch die erste Schnittstelle ihren Anforderungen entsprechend zu behandeln. Darüber hinaus sollen Anforderungen der Prozessindustrie mit denen der Abfallwirtschaft verglichen werden, um einen dort bestehenden Aufklärungsbedarf zu erfüllen. An Praxisbeispielen sollen Missverständnisse aufgeklärt werden. Insbesondere sollen bisher nicht beseitigte Fehler in der Planung von Anlagen der Abfallwirtschaft durch Hinweise aus der Prozessindustrie aufgezeigt und zukünftig vermieden werden.

Verfahrenstechnische Prozesse werden von der Reaktionsgleichung über Apparaturen, Teilanlagen bis hin zur komplexen Produktionsanlage dargestellt, um ein Schnittstellen übergreifendes Verständnis für den zu automatisierenden Prozess herzustellen. Grundlage sind in der Praxis erworbene langjährige Erfahrungen der Planung, Projektierung und Seminardurchführung in der Kraftwerksleittechnik, Prozessleittechnik der Chemie und Nahrungsmittel-Herstellung, der Abfallwirtschaft und Erfahrungen im Einsatz betriebswirtschaftlicher Software-Systeme. Aus praktischen Anforderungen der Abfallwirtschaft heraus entstanden im Buch dargestellte Prozessleittechnik-Konzepte, die als Grundlage für weitere prozesswissensbasierende Planungen dienen können.

Die Zielgruppe dieses Buches sind auf dem Gebiet der Verfahrens- und Prozessleittechnik der Prozessindustrie und Abfallwirtschaft tätige Ingenieure, Techniker, Meister und Facharbeiter sowie Studenten an Universitäten und Hochschulen.

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