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APPLICATION OF WATER CYCLES IN CERAMIC INDUSTRY

The problems related to water and wastewater disposal in ceramic industrial works and some achievements in this respect have been discussed. A considerable increase in the demand for water observed recently in the ceramic industry is caused by concentration of production and application of "wet" dust removal devices recently in the ceramic industry. The increase in water demand has often made some troubles with water supply in ceramic industrial works. The two-step wastewater purification method which has been developed and applied implement has allowed to use of the reclaimed water for the auxiliary needs in production. Further progress in this field will be possible after application of the three-step method of wastewater treatment. The quality of the reclaimed water will be the same as correspond to that required from technological water. Thus it is possible to close the cycle so that fresh water could be used only to complete the losses.

1. INTRODUCTION

The technologies applied in ceramic industry are not excessive in their water demands. The amounts of water used are ca. 0.6% of the total amount of water consumed by the all industries in this country. However, the recent growth of production and the modernisation of the equipment in the ceramic works occurring recently have considerably increased the water demand for the technological processes and for the auxiliary needs. The introduction of new technologies and equipment have also contributed to the increased water demand. A significant increase in water demand is moreover, connected with new dust-removal installations collecting pollutants in water.

All these factors caused the growth of water consumption index calculated for a production unit in all the types of the ceramical works. In the whiteware ceramics works this index increased from 10–20 m^3/Mg of the production few years ago [5] to 45–50 m^3/Mg. In this situation the output of water intakes in the majority of works could not meet the needs of the constantly growing water demands and in some cases it became the limiting factor of production growth especially, when water could not be supplied from other sources. This forced the specialists to reuse water in greater scale than it was used till now.

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In connection with this problem several research works in the field of water wastes balance have been carried out in Poland during the last few years which enabled a further progress in the methods of industrial wastes treatment combined with the water reuse.

2. THE QUALITATIVE AND QUANTITATIVE CHARACTERISTIC OF WATER FOR PRODUCTION NEEDS

Considering of the existing-designing and utilisation-practice, the following indices of water consumption can be assumed for production needs in each branches of the ceramic industry [2], [5], (table 1). The lower limits of these indices refer to the existing and modernised works, the upper to the works designed. Water consumption index depends also on the air cleaning method used in the dust removal installations. When "wet" dust removal devices are used, the upper values are obligatory.

Table 1

Type of production	Water consumption index for production unit (m^3/Mg)
Ceramic whiteware	15–20
Sanitary ware	6–15
Stone-ware goods	2–10
Glazed tile — dry method	0.5–2
Glazed tile — wet method	4–8
Enrichment of ceramic raw materials	3–5

The quantity of water demand for production needs in ceramical works are best characterised by the values given in table 2. The values presented refer to the demand of fresh water. They take into account the closed cooling water cycle and the fact that the demand for water used for auxiliary needs is met by the water reclaimed from the purified industrial wastes.

Chemical composition of water is used for technological needs in ceramic industry has a great influence on the quality of products. The industry practice shows that technological troubles and changes in the qualitative parameters of ceramic body and semi-finished products are very often caused by the changes in the quality of water applied.

It has been stated that a substantial influence on the total mineralization and the concentration of individual ions in used water have the properties of the ceramic body. During the production process the highest possible concentration of solid phase is to be achieved in the casting slip and the appropriate viscosity, allowing to obtain the right casting parameters.

Table 2

Type of the production plant	Production Mg/a	Daily demand m^3
Whiteware ceramic-plant	10 000	1 100
Semi-vitreous China ware plant	10 000	800
Sanitary ware plant	12 000	450
Sewerage stone-ware plant	75 000	600
Glazed tile plant	5 000 000*	750
Ceramic raw-material enrichment plant	200 000	2 500

*) m^2/a

An unfavourable influence in this respect is exerted by too high concentration of magnesium salts, especially of its chloride, on the ceramic body, mainly on the China body.

Too high concentrations of calcium chloride and sodium salts in technological water reduce the concentration of the solid phase, especially in the semi-vitreous and faience body. The smallest influence on the casting processes is exerted by calcium sulphate, which precipitates when the concentration of electrolytes in the solution increases, especially due to the addition of the fluidization agent (soluble glass) to the ceramic body.

Some ion composition in water can influence favourably the body fluidization process and at the same time affect unfavourably the filtration which is the second very important process in the technological cycle of ceramic goods production. In view of the above it is necessary to determine the optimal chemical composition of water.

The influence of the ion composition of water on some of parameters of the ceramic body are presented in table 3. Too high concentrations of calcium and magnesium salts in the ceramic body causing water hardness are responsible for negative effects on the bisquit firing process. These salts concentrated in the definite sites of the product, melt during the

Table 3

Ion	Concentration	Viscosity	Thixotropy	Casting velocity	Strength
Ca^{+2}	to 150	considerably increases	increases	increases	decreases
Mg^{+2}	to 80	increases	considerably increases	increases	slightly decreases
$Na^{+}+K^{+}$	to 100	considerably decreases	decreases	decreases	slightly increases
$SO_4^{-2}+C^{-2}$	to 500	considerably increases	increases	considerably increases	increases
$HCO_3^{-}+CO_2$	to 400	increases	considerably increases	increases	decreases

firing process (1350°) and forming efflorescences which being not covered in the glazing process deteriorate functional quality and aesthetic properties of the goods. Iron compounds have also unfavourable influence on the ceramic body. Too high concentrations of these compounds reduce the whiteness of the products. The research work [6] and many years' experiments in production have allowed to determine the quality-requirements for technological water presented in table 4.

Table 4

Quality indicator	Units	Types of the produced goods		
		China ware	Semi-vitreous ware	Faience
Solid residue	mg/dm^3	500	400	400
Organic suspension	mg/dm^3	20	10	10
Reaction	pH	6.5–8.0	7.0–8.0	7.0–8.0
Total hardness	$mval/dm^3$	3.6	2.85	2.85
	°n	10	8	8
Carbonate hardness	$mval/dm^3$	0.71	0.71	0.71
	°n	2	2	2
$Ca^{2+}+Mg^{2+}$	mg/dm^3	60	40	40
$SO_4^{2-}+Cl^-+NO_3^-$	mg/dm^3	250	150	200
Fe^{3+}	mg/dm^3	0.3	0.3	0.3

3. WATER CYCLES USED AT PRESENT IN THE CERAMIC INDUSTRY

The ceramic industrial works have a mixed system of water supply, their water demand is covered by partially and fully closed cycles. The latter is used for the equipment cooled with water. Small water losses in the open cycle (4–7% of total amount of circulating water) are compensated up with fresh water. The cooling cycle supplies such units as tunnel kiln fans, air compressors, vacuum pumps, etc.

In the partially closed cycle there one uses water, reclaimed from the industrial wastes. This water can be used to

supply the washers for air cleaning,

wash technological pipelines for transport to agitate solid and plastic waste materials,

— wash tile floor, containers etc.

It can be said, that the water demand for auxiliary needs in the whiteware ceramic works, sanitary goods works and in the faience tile works can be covered with reclaimed water. The demands of mentioned above units for technological water constructed sometimes even 60% of water consumption in the given factory.

The situation in porcelain clay processing works is a bit different. A part of the waste-water can be used without treatment in raw material segregation processes. The purified industrial wastewater can be used first of all to compensate the losses in water cycle in the sand-production line.

The technological units which are used to body and glaze preparation, to finishing processes of the goods and to production of gypsum moulds are supplied with water in an open cycle. This makes about 30–40 % of the total demand for technological water in the given plant. So far the quality of the purified wastewater has not allow to use the reclaimed water for technological needs. In the opened water cycles there are moreover some irreclaimable losses (drying and fitting of products losses) which are estimated at about 40 % of consumption. The reuse of water in the ceramic industry has already a 20 year old tradition. It was initiated with the repeated use of water coming from the filter presses, used in most the ceramical works to dehydrate the mass. The amount of water reclaimed was small and made only 10 % of the industrial water demand. Nevertheless in many works water reclaiming units have been gradually installed. In the beginning of the 70-s a succesful two-step wastewater purification method was developed for this branch of industry [4].

This method enabled a 99 % reduction of suspended matter in the wastewater, and considerably extended the possibility of the reuse of purified wastewater. This, in turn, made it possible to arrange a mixed water supply system in some plants. It was just the purified wastewater, which covered water demand for auxiliary needs of production in several works (fig. 1). The amounts of the reclaimed water used in the ceramic industry is presented in table 5. The possibility of the application of the so-called small closed cycle of water,

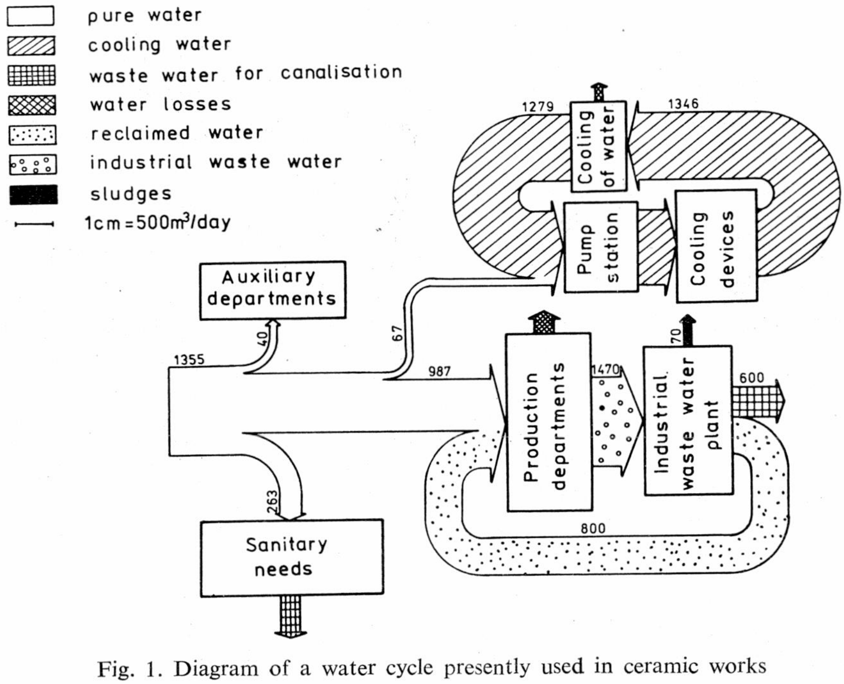

Fig. 1. Diagram of a water cycle presently used in ceramic works

Rys. 1. Schemat obiegu wody stosowanego obecnie w fabryce ceramicznej

Table 5

Production plant	The amount of the used industrial wastewater m^3 per day	% in the total amount of the industrial wastewater
ZPS Lubina	240	60
ZWS Krasnystaw II	310	65
ZPS Wałbrzych — being built	800	57
ZPSK „Maria III" — being built	920	31

supplying the washers when hydrocyclones for separation of solid wastes from liquids were used has been also examined. A combination of washer- hydrocyclone with the required fitting gurantees a repeated use of the same water. Further utilization of the purified industrial water in this branch of industry is connected with the need of more efficient purification methods than those nowadays used.

4. THE POSSIBILITIES OF CLOSED WATER CYCLES IN CERAMICAL WORKS

The so far employed wastewater purification methods, consisting in sedimentation and coagulation with help of inorganic coagulants are becaming inadequate because of the water protection, in case when the wastewater is carried away to surface water as well as of the possibility of repeated use of the purified wastewater.

An attempt to estimate the parameters of highly efficient treatment of ceramic wastewater was carried out in the Institute of Environment Protection Engineering of the Technical University of Łódź. For crude wastewater with very high pollution indices, (inorganic suspensions and turbidity), a multi-step purification system has been proposed. It comprises natural sedimentation, flocculation with synthetic polyelectrolytes, after-coagulation sedimentation and filtration. The application of suitable parameters allows to obtain high purifiction effects with relatively low capital costs.

The research works, which were carried out in a quarter technical scale (in the test station) at the Sanitary Ware Works at Koło allowed to verify the usefulness of the method proposed under normal work conditions of a production plant. In the water reclaimed after the last step of wastewater treatment total suspentions ranged within 10.0–0.0 mg/dm^3, the turbidity was almost equal zero, the hardness equaled 2.6–3.3 mval/dm^3, the concentration of anion chloride waned within 20–75 mg/dm^3, and that of sulphate ion within 120–145 mg/dm^3.

From comparison of the results obtained with the qualitative requirements for technological water (table 4) it follows that the values are convergent or they need a small correction. The correction of the water parameters (e.g. the concentration of sulphates, chlorides and the hardness) can be obtained by supplying the fresh water prepared by the water conditioning station. This is also necessary because of the quantitative balance of water in the cycle. In the mass balance for the system presented in fig. 2 we can use a dependance,

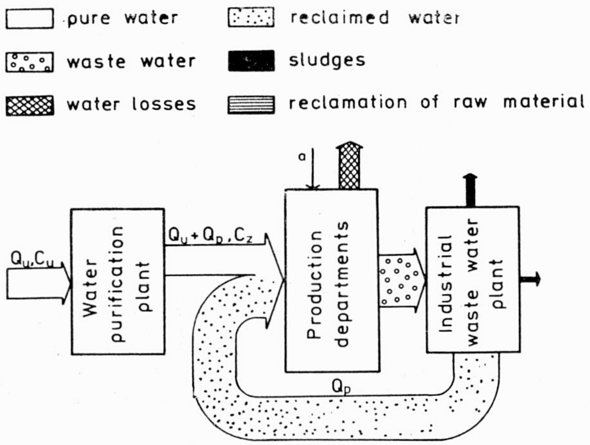

Fig. 2. Diagram of the proposed technological water cycle in a ceramic work

Rys. 2. Schemat proponowanego obiegu wody w fabryce ceramicznej

which shows the concentration of the chosen indicator, which characterises the quality of water as a function of the quantity and quality of the added water

$$C_i = C_s + \frac{1-k}{k}\left(\frac{a}{Q_s+Q_r}\right) \tag{1}$$

where

C_s — the concentration of the chosen quality indicator of supplementary water,

a — the load of the relected indicator, passing to the cycling water during one cycle,

Q_s+Q_r — the amount of water, which covers, the technological demands of the production plant,

Q_s — the amount of the supplementary water,

Q_r — the amount of the reclaimed water,

k — the water supplement index.

The index k defines the ratio of supplementary water to the amount of water used for technological needs in the production plant

$$k = \frac{Q_s}{Q_s+Q_r}. \tag{2}$$

As an example of the relations (1) and (2) with respect to anions ($SO_4^{2-} + Cl^- + NO_3^-$), assuming that their concentration in feed water is 100 mg/dm^3 are presented graphically

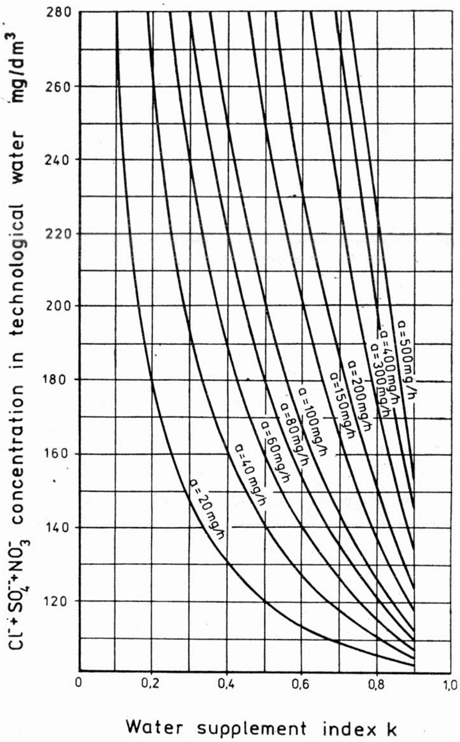

Fig. 3. The concentration of salts dissolved in industrial water vs. the index of fresh water supplement for different unit loads of the dissolved salts which go through to the circulating water during one cycle — *a* (presumed concentration of ions $Cl^- + SO_4^{--} + NO_3^-$ in make-up water Cu = 100 mg/dm³)

Rys. 3. Zależność stężenia soli rozpuszczonych w wodzie technologicznej od stopnia uzupełnienia świeżą wodą dla różnych jednostkowych obciążeń nierozpuszczonych soli, które przechodzą do wody obiegowej w ciągu jednego cyklu — *a* (założone stężenie jonów $Cl^- + SO_4^{--} + NO_3^-$ w wodzie uzupełniającej Cu = = 100 mg/dm³)

in fig. 3. Knowing the unit load of the indicators passing to the cycling water during one cycle — *a* (mg/h) we can estimate the amount of the supplementary water in the cycle and the corresponding concentration of the anions in the feed water.

The possibilities of the repeated use of water are confirmed by the investigations on the mineral raw materials processing and refining-processes, performed at the Technical University of Warsaw. The tests were made without supplementing the cycle with fresh water. The effluents after the production processes were purified by coagulation and sedimentation. The wastewater was coagulated with calcium and aluminium sulphate in presence of a small amounts of non-ionic polyelectrolyte. After 10–15 repeated use of the reclaimed water the concentrations of sulphates and chlorides, water hardness and the general mineralization of water were increased. This excluding, however, the possibility of the use of the reclaimed water in the next cycle of the investigated operation of production process. We can assume that the application of the new method for the wastewater treatment [3] and of the proposed method for the estimation of the concentration of the water quality indicators by choosing the right value of the index of water supply allows to obtain the required ranges of these limit values.

As it follows from the situation described these methods can be now applied to a closed industrial water cycle in the ceramic works when fresh water would be used only to compensate the losses.

5. THE RESULTS

1. The usefulness of the reclaimed water obtained from industrial wastewater for the production and auxiliary needs depends on its quality.

2. The methods of industrial wastewater purification so far used enable a repeated use of water for auxiliary needs.

3. In several realized and designed ceramical works the amount of water repeatedly used is about 60% of the total amount.

4. The recenty developed three-step industrial wastewater purification methods, which ensuring a total purification and the estimation of the qualitative parameters of water for technological needs, does extend the applicability of reclaimed water in greater amounts in fully closed water cycle.

5. The amounts of supplementary water should depend on its losses in the production processes and also on the indispensible correction of the quality of supplying water.

6. The worked out method allows to reduce the consumption of fresh water an essential ceramical industry and to discharge the wastes to rivers in extraordinary cases only.

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MOŻLIWOŚCI STOSOWANIA ZAMKNIĘTYCH OBIEGÓW WODNYCH W ZAKŁADACH PRZEMYSŁU CERAMICZNEGO

W ostatnich latach nastąpił znaczny wzrost zapotrzebowania na wodę w zakładach przemysłu ceramicznego, spowodowany koncentracją produkcji i zastosowaniem „mokrych" urządzeń odpylających. Wzrost wskaźników zużycia wody powodował niejednokrotnie kłopoty z zaopatrzeniem tych zakładów w wodę. Skład chemiczny wody używanej do celów technologicznych ma duży wpływ na jakość produktu.

Stwierdzono, że nierzadko trudności technologiczne i wahania parametrów jakościowych mas ceramicznych są spowodowane niekorzystnymi zmianami jakości stosowanej wody.

W artykule określono wpływ stężenia poszczególnych jonów występujących w wodzie na własności mas ceramicznych oraz przedstawiono wymagania jakościowe dla wody technologicznej. Przedstawiono również typy obiegów wodnych stosowanych obecnie w przemyśle ceramicznym.

Wprowadzenie zamkniętego obiegu wody technologicznej związane jest z doborem właściwego sposobu oczyszczania ścieków i odzysku wody.

Przedstawiono opracowaną i wdrożoną dwustopniową metodę oczyszczania ścieków, która pozwoliła wykorzystywać odzyskaną wodę w produkcji. Dalszy postęp w tej dziedzinie stanowi trzystopniowa metoda oczyszczania ścieków, której zastosowanie pozwala uzyskać wodę o jakości odpowiadającej wymaganiom stawianym wodzie technologicznej.

Skorygowanie parametrów wody zasilającej można uzyskać przez uzupełnienie obiegu wodą świeżą przygotowaną w zakładowej stacji uzdatniania. Istnieje realna możliwość zamknięcia obiegu wody przemysłowej tak, aby tylko straty były pokrywane wodą świeżą.

WASSERKREISLÄUFE IN KERAMISCHEN BETRIEBEN

In keramischen Betrieben steigt der Wasserbedarf ständig an, da immer mehr nasse Entstaubungsverfahren zur Anwendung kommen. Es ist einsehbar, daß technologische Schwierigkeiten, die mit der Güte der keramischen Masse zusammenhängen, auf die Qualität der benutzten Wassers zurückzuführen sind. In diesem Zusammenhang wird die Aufstellung von entsprechenden Richtlinien gefordert, da spezifische Ionen die Wassergüte beeinträchtigen.

Die Schließung von Wasserkreisläufen ist sowohl von den Abwasserreinigungs verfahren wie auch von den Wasseraufbereitungsmethoden abhängig. Im Beitrag wird eine bereits in Betrieb genommene zweistufige Abwasserreinigung beschrieben, die die Benutzung des gereinigten Abwassers für verschiedene Zwecke möglich machte. Die Erweiterung der Anlage um eine zusätzliche Stufe, wird eine volle Rückgewinnung und die Beimischung in die keramische Masse dieses Wassers ermöglichen. Lediglich die Verluste sollen mit Frischwasser ergänzt werden.

ВОЗМОЖНОСТЬ ПРИМЕНЕНИЯ ЗАМКНУТЫХ ЦИКЛОВ ВОДЫ НА ЗАВОДАХ КЕРАМИЧЕСКОЙ ПРОМЫШЛЕННОСТИ

В последние годы наблюдается значительное увеличение потребности в воде на заводах керамической промышленности, вызванное концентрацией производства и применением „мокрых" обеспылевающих устройств. Повышение показателей потребления воды вызвало значительные затруднения в снабжении этих заводов водой. Химический состав воды, используемый для технологических целей имеет большое влияние на качество воды.

Выявлено, что часто технологические трудности и колебания качественных параметров керамических масс вызываются неблагоприятными изменениями качества используемой воды.

В статье определено влияние концентрации отдельных ионов, выступающих в воде, на свойства керамических масс, а также представлены качественные требования для технологической

воды. Приведены также типы циклов воды, применяемых в настоящее время в керамической промышленности.

Введение замкнутого цикла технологической воды связано с подбором правильного способа очистки сточных вод и регенерации воды.

Предложен разработанный и внедрённый двухступенчатый метод очистки сточных вод, который позволил использовать регенерированную воду для вспомогательных целей производства.

Дальнейший прогресс в этой области представляет собой трёхступенчатый метод очистки сточных вод, применение которого позволяет получить воду качества, соответствующего требованиям, предъявляемым к технологической воде.

Откорректировать параметры питающей воды можно путём пополнения цикла свежей водой, подготовленной на заводской станции водоподготовки.

Существует реальная возможность замкнуть цикл производственной воды таким образом, чтобы только потери возмещались свежей водой.