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Effectiveness of Sorbents for Reducing the Content of Nickel Cations in Water

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Abstract : The presence of heavy metals in waters is a relatively frequent manifestation of their pollution. The big danger with these metal elements is the fact that they are already highly toxic at very low concentrations. The use of ion exchange and sorption is one of the possible methods of the removing metals from water. Considering the economic aspects of such a process, the possibilities of using easily available natural materials, including zeolites are being sought. Zeolites belong to hydrated aluminosilicates with a regular tetrahedral structure. The aim of the work was to study and compare the sorption properties of natural and synthetic zeolite. The experiments were related to the reduction of the content of nickel cations from model aqueous solutions.

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1 Introduction

Heavy metals and their compounds burden the environment with no hope of their natural degradation. In waste water treatment plants, heavy metal ions are removed by oxidation-reduction reactions, coagulation and sedimentation, sorption on activated carbon, ion exchange on ion exchangers. The coagulation process followed by filtration, membrane processes and ion exchange are commonly used methods for cleaning water. Due to economic aspects, methods are sought that are cheaper, but at the same time highly effective. Adsorption methods have proven to be very effective, economically interesting and easy to operate. The sorption and ion exchange properties of zeolites are interesting from the point of view of treatment of drinking and waste water. Zeolites have been extensively studied with a focus on applications in such technological areas as catalysis, ion exchange and sorption. The possibilities of using zeolites result from their structure. Zeolites are microporous aluminosilicates with a microporous structure, high crystallinity, and a large surface area. The wide range of their technological applications results from the excellent thermal and chemical stability of these materials, their large surface areas, the availability of various topologies and versatile chemical properties.

2 Properties of the Zeolites

Zeolites play an important role as ion exchangers and sorbents due to their high affinity towards heavy metals and their ion-exchange capacity. Synthetic zeolites of the NaY and Y type, as well as natural zeolites, are among the applicable zeolites for water treatment to remove heavy metal ions. Clinoptilolite and mordenite are the natural zeolites often used in practice. Zeolites have a three-dimensional structure formed from tetrahedra $[SiO_4]^{-4}$ and $[AlO_4]^{-5}$ [1,2,3,4].

Tetrahedrons create simple formations in the zeolites that are regularly repeated throughout the structure of a given structural type of zeolite and create secondary building units (SBU). Different ways of connecting tetrahedra create different types of secondary units. By spatial joining of individual types of secondary building units creates a three-dimensional structure, characteristic of each zeolite structure. Each zeolite structure is marked with a three-letter code, e.g.

clinoptilolite belongs to the structural type HEU, characterized by the structure of natural zeolite - heulandite. The basic framework of zeolites consists of a network of $[SiO_4]^{-4}$ tetrahedra, in which part of the silicon atoms is isomorphously replaced by aluminum atoms. The negative charge that arises is compensated by mobile cations of alkali metals or alkaline earth metals [2,3].

Channels of precisely defined dimensions are created inside the crystalline system of zeolites, in which these cations are located. An important property of zeolites is the ability to exchange these cations for cations that are found in the surrounding external environment, i.e. also in the water environment. Cations of heavy metals removed from aqueous solutions are immobilized on zeolite by two mechanisms - ion exchange and chemisorption [4]. In the ion exchange process, cations with an oxidation number of one, which have a smaller hydrated ion radius, and cations with a lower enthalpy are more mobile. Zeolites can be represented by the structural formula based on a crystallographic unit cell:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$$

where n represents the valence of a cation M, w is the number of water molecules per unit cell, x and y is the number of tetrahedra per unit cell, and the y/x ratio is most often in the range of 1 to 5 [5,6]. Zeolites retain their structure in a wide range of pH, from 1,0 to 11,5. Natural zeolites acquire new, original properties through chemical treatment, e.g. their surface increases, sorption capacity increases, physicochemical and mechanical properties improve. This enables the use of natural zeolites in a wide range of applications. Their advantage over synthetic zeolite is better heat resistance and lower price. Among the applications of natural zeolites, their use for energy transfer in energy conversations and heat exchange systems is noteworthy [7,8,9].

The wide range of their technological applications stems from the excellent thermal and chemical stability of these materials, their large surface areas, the availability of various topologies and versatile chemical properties.

3 Experimental

In order to design the arrangement of the cleaning process by sorption on a solid layer, it is necessary to know the kinetic course of sorption. This article presents a laboratory experiments to determine the sorption parameters and the kinetic course of sorption of nickel cations on natural zeolite clinoptilolite, which is an inexpensive and ecologically harmless sorption material. The course of sorption was compared with sorption on synthetic zeolite. Natural zeolite clinoptilolite and synthetic zeolite calcite were used as sorption material for the experiments. The nickel cation concentration was determined on a Optima DIGITAL COLORIMETER Model AC 114 photometric analyzer (Optima, Tokyo, Japan). Measurements were taken at a wavelength of 660 nm. The mass concentration of nickel cations was determined by the calibration curve method.We used chemicals of analytical purity to prepare model samples. Model samples with a concentration of 2,23 $g\cdot dm^{-3}$ nickel cations were used in this experiment. Samples of sorbents weighing 40g were used for sorption.The tested sorbents were natural clinoptilolite with a grain size of 1,0-2,5 mm and synthetic zeolite calcite with a grain size of 3 mm. Calcite is a synthetic zeolite type 5A with a pore size of 0,5 nm. Its chemical composition in the dehydrated state the formula $CaO\cdot Na_2O\cdot Al_2O_3\cdot 2SiO_2$ expresses. Laboratory measurements were aimed at studying the kinetic course of sorption of nickel cations on natural zeolite - clinoptilolite with a grain size of 1,0 mm – 2,5 mm originating from Nižný Hrabovec, and on synthetic zeolite - calcite. We performed ion exchange sorption from a model sample of inorganic salts of nickel cations at the solid interphase interface of the mentioned sorbents. By testing two types of sorbents, we monitored the kinetic course of sorption and found out the necessary parameters of sorption, namely the sorption capacity of individual sorbents, the equilibrium concentration and the partition coefficient. We also calculated the efficiency of both sorbents. For the sorption of nickel cations, we used a model solution with an initial mass concentration of 2,23 $g\cdot dm^{-3}$. In order to define the time needed to stabilize the equilibrium in the system, the dependence of adsorbed amount on the time of contact of adsorbent with adsorbate was observed. Experiments realised at a temperature of 21ºC. The course of sorption in all model samples was monitored in precise time intervals. With increasing contact time of the sorbent with the solution, the concentration of nickel cations in the solution asymptotically approached the equilibrium concentration c_{eq}. Measured values are in the table 1. For the qualitative expression of adsorption, it is necessary to know the amount of substance or weight adsorbed by the adsorbent weight unit. The specific adsorption of a particular component can be expressed according to (3.1) [10,11,12].

$$a = \frac{c_0 - c_{eq}}{m} \times V \qquad (3.1)$$

where a is the equilibrium adsorption capacity of adsorbate, V volume of the solution in contact with the adsorbent, m mass of adsorbent, c_0 initial concentration of adsorbate in solution, c_{eq} concentration of adsorbate during equilibrium.

Measurements were carried out five times, the average value was used for calculations. From the measured values, we calculated the standard deviation according to the formula:

$$\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - x_{priem)^2}} \tag{3.2}$$

Table 1 Change in the concentration of nickel cations over time on clinoptilolite and calcite in a solution with an initial concentration of 2.23 g.dm^{-3}

Time [min]	30	60	90	120	150	180
Clinoptilolite c [g.dm^{-3}]	1.71	1.62	1.45	1.3	1.2	1.2
Calcite c [g.dm^{-3}]	0.05	0.01	0.01	0	0	

Using formula 3.1 to calculate the sorption capacity, we determined the sorption capacity of clinoptilolite with respect to the sorption of nickel ions 6.437 mg.dm^{-3} and calcite 13.901 mg·dm^{-3}.

Table 2 Amount adsorbed on the clinoptilolite and on the calcite as a function of time

Time [min]	30	60	90	120	150	180
Clinoptilolite a [mg.dm^{-3}]	3.25	3.8	4.69	5.81	6.4	6.4
Calcite a [mg.dm^{-3}]	13.6	13.9	13.9	13.94	13.94	

Figures 1 and 2 graphically show the kinetic course of sorption on clinoptilolite and calcite.

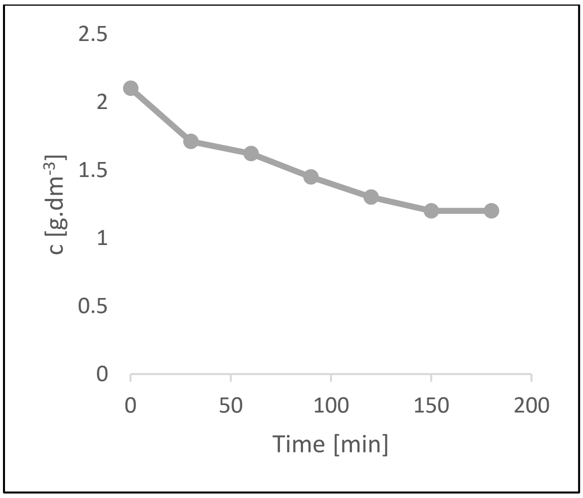

Figure 1 Decrease of nickel cations in the solution using clinoptilolite

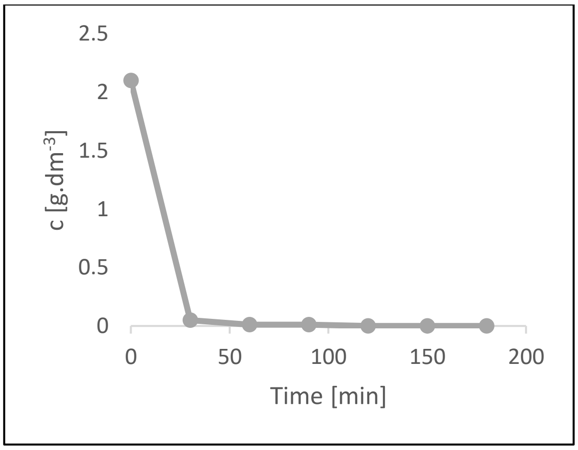

Figure 2 Decrease of nickel cations in the solution using calsitecalsite

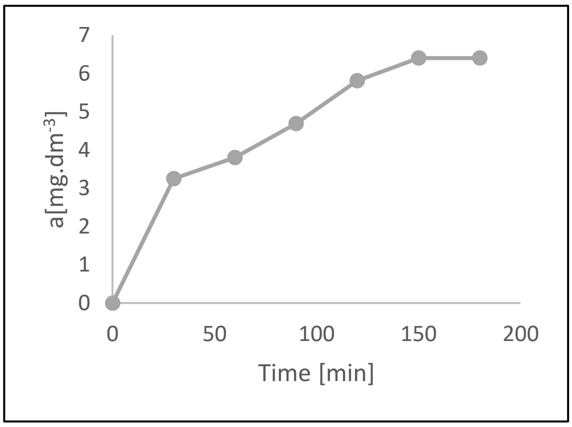

Figure 3 Kinetic of sorption using clinoptilolite

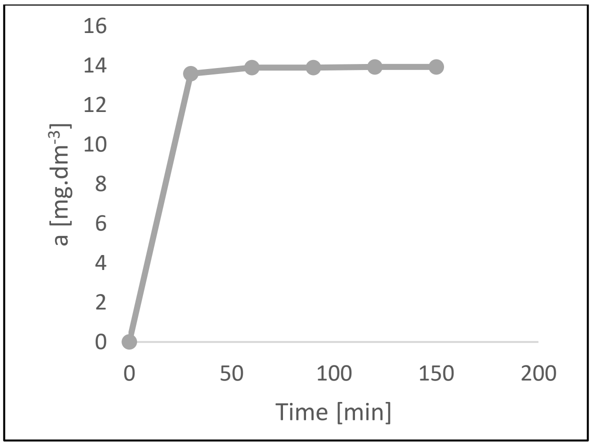

Figure 4 Kinetic of sorption nickel cations using calsite

The quantitative distribution parameter of the substance between the solid and the liquid phase is the K$_d$ partition coefficient [13]. The importance of determining partition coefficients lies in the fact that they belong to the basic input data in mathematical models of the transport of monitored substances in water. We calculate the distribution coefficient K_d according to the equation:

$$K_{d}=\frac{c_0-c_{eq}}{c_{eq}}\times\frac{V}{m} \tag{3.3}$$

Based on this calculation, the K_d coefficient for clinoptilolite was 0.005 and the K_d coefficient for calcite was 1.332.

The maximum adsorbed amounts a_i were calculated for each equilibrium concentration, while the magnitude of the error was expressed by the standard deviation according to equation (3.2) S=0.0478 and 0.062.

According to equation (3.4), we calculated the efficiency of clinoptilolite in reducing the concentration of nickel cations in aqueous solution.

$$\eta = \left(\frac{c_0-c_{eq}}{c_0}\right) \times 100 \tag{3.4}$$

We recorded a higher efficiency on the synthetic zeolite calcite, namely 99,5%, while on the natural zeolite, clinoptilolite, an efficiency of 46,2% was achieved.

4 Conclusion

Unlike amorphous organic ionic compounds, natural zeolites have a solid skeleton formed by polyoxides of silicon and aluminum, a sufficiently large adsorption surface, they are hydrophilic, polar, microporous, heat and radiation resistant, affordable, and they exhibit lower abrasive properties than activated carbon, which predetermines them for more suitable hydrodynamic use in practice. Compared to synthetic zeolites, however, natural zeolites have a significantly lower sorption capacity. Therefore, it is necessary, natural zeolite modified for wider use. With the current ecological problems with maintaining the cleanliness and health acceptability of the components of the environment for nature and man, the modification of natural ion-exchange materials is coming to the fore with the aim of using them mainly in cleaning or treatment of various types of waste water. By chemical treatment, zeolites acquire new, original properties, e.g. their surface increases, sorption capacity increases, physicochemical and mechanical properties improve. The subject of further research will be the modification of clinoptilolite into a monoionic form and the increase of its sorption capacity, and thus its efficiency with respect to heavy metal cations.

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Efficiency Possibilities of Energy Management of Apartment Building – Use Case

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Abstract : In this paper we are assessing the aspect of ecological renovation of typical apartment building in Slovakia from energy, ecology and user comfort point of view. For increase in energy efficiency of the building we propose to install photovoltaics on the roof and south facing façade with capacity of 45k Wp, heat pumps for utilization of waste heat from the building's sewage system and waste heat from ventilation shafts with total capacity of 50 kWp, external window shading for east, west and south facing façades, green roof and ceiling cooling for apartment units. The complex renovation represents a positive benefit not only from the user, energy and environmental point of view, but also economical.

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1 Introduction

Energy market is constantly developing dynamically. Objectively, the global disproportion between energy production and consumption is growing, the need to change the energy system in practically any sector of the economy is increasingly being discussed. The legitimate demand for the use of alternative and renewable energy sources is increasingly being applied. In the case of heating, this means that it is not enough to use a highly efficient energy source, but it is necessary above all to reduce the heat loss of the building and make the heat distribution system more efficient.

When choosing a suitable method of supplying heat to apartment buildings, the first priority is finding a compromise between costs and user comfort. A reduction in heat production and distribution costs can be achieved either by reducing energy consumption by replacing an old source with a more modern one, or by completely changing the heat source, while this does not necessarily mean a deterioration in thermal comfort. Modern methods of heating allow for a choice based on individual needs and economic possibilities, while allowing to completely or partially replace the original source with a renewable one. However, it is always necessary to respect the requirements of consumers, society and environmental protection.

Apartment buildings represent a certain specificity from the point of view of the use of RES. This is primarily due to the way the building is owned and the way energy costs are calculated. These two factors significantly influence the decision on the type of renewable resource that will be used in the apartment building. In most cases, the heat is supplied to the building centrally, so a solar system for heating support, a heat pump and, in very specific cases, a boiler for wood fuel (pellets, wood chips) come into consideration as a renewable source of heat production.

In the presented work, technologies for the production and supply of heat for heating and preparation of hot water, as well as technologies for the supply of cold, are assessed in accordance with advice of experts in the field of energy and architecture with representatives of the client. The goal was to harmonize the technical and technological possibilities with the requirements and possibilities of the residents of the apartment building under consideration.

2 Theoretical analysis of the topic

If you are interested in reducing the operating costs of an apartment building, a number of solutions are currently available not only for the efficiency of consumption, production and distribution of electricity, heat and cold, but also for various possibilities of their mutual combination. Likewise, various solutions for retaining water in the building and its surroundings are available today, either through retention technologies, green architecture, or a suitable combination of them.

An important factor when considering the energetical reconstruction of the building is to find out the interest of the owners of apartments and non-residential premises in the extent of changes. The scope of the changes does not only mean their economic impact, but also their impact on the way the building is used and, last but not least, their impact on the climate around the building and thus the overall climate. In this context, it is important to realize that some measures designed primarily to increase the user comfort of housing may not lead to a reduction in operating costs.

The measures that were assessed in the study are therefore a combination of measures aimed primarily at:

- reducing the amount of purchased thermal and electrical energy,
- reduction of OPEX,
- increasing the comfort of using the building and apartments,
- reducing the negative impacts of the use of the building on its surroundings.

The design part of the study is divided into a part in which individual variants are assessed separately. This means as if the technologies and measures were installed and implemented independently.

In the second part, variants are assessed, in which the measures selected based on discussions with representatives of the apartment building are combined into the resulting energy-material mix. In this case, the economics of investment and operating costs are assessed considering the interrelationships between individual technologies.

The above means that while, for example, the return of the installation of a photovoltaic system or a heat pump alone represents a certain value, in a mutual combination the amount of return will be different, as, for example, a heat pump can consume electricity produced by a PV system [1] .

In the current situation on energy market, we recommend the use of heat sources based on renewable energy from an economic point of view and from the point of view of environmental impacts. In this way, it is possible to reduce emissions of the main pollutants in the city and increase the efficiency of heat production [2-5] .

We recommend the same procedure in the case of family, apartment buildings and administrative buildings in the city. The main recommendation is to create a comprehensive concept of building management by considering all related elements, such as in the case of energy:

- energy management,
- energy efficiency of heat and electricity production with an emphasis on increasing the share of RES,
- energy efficiency of heat consumption – insulation, regulation, replacement of distribution systems, etc.
- participation of the heat supplier in the efficiency and greening of energy production and consumption,
- green architecture,
- complex energy mix,
- education and more.

The main coordinating and controlling element of the new energy architecture of the building should be an effective system of energy or facility management.

3 Analysis of the state of the issue

The subject of the study is a twelve-story apartment building with 48 residential units. The apartment building has been insulated between 2006 and 2007, with the renewal of apartment windows and common areas.

The territory is exposed from the point of view of geomorphology, which is advantageous from the point of view of the use of solar energy, on the other hand, the increased windiness of the territory is the reason for more intensive cooling of the building.

3.1 Current status

The data on thermal technical condition of the apartment building are based on the project documentation of the building. Data on heat gains from solar radiation are important from the point of view of assessing the possibilities of reducing heat gains by shading elements in the summer season. Project assessment of building is important from the point of view of assessing the use of the building by its inhabitants and from the point of view of assessing the possibilities of energy savings.

The apartment building was insulated in 2007, since then the projected need for heat has not exceeded the actual consumption even once.

3.1.1 Heating and hot water preparation

We obtained the real consumption of the building from the billing data for the years 2016-2017 and from the supplied data for the year 2019. The average yearly consumption was 203 600 kWh.

Table 1 Heat consumption

Year	Heat consumption (kWh per year)	Unit cost (€/kWh)	Total cost (€ per year)
2017	214500	0.081	17335
2018	202861	0.089	18126
2019	193528	0.098	18930
Yearly average	203630	0.089	18130

From the point of view of the users of the apartment building, there are questions about the effectiveness of the funds spent on improving the building's energy efficiency. Projecting the efficiency of the energy economy of the building itself is practically impossible from the point of view of calculating the return on investment. This is because it depends on the price of heat and energy that the owners buy from the supplier, which does not have any long-term price policy models established by referring to the law.

Currently, the disadvantage for consumers is also the fact that they do not have legal option of disconnecting from the central heat source. This results in the fact that even in the case of using another source of heat, for example a renewable one, the customer is forced to obtain a certain amount of heat from central supplier and pay associated fixed fees.

At the moment, fees for heating systems are in the ratio of 1.35:1, expressed in numbers, this means that residents pay an average of € 11,130 per year for the installed capacity, regardless of consumption. They pay an average of € 8,200 per year for it. In the case of using an alternative heat source, it is therefore necessary to ensure a reduction of the fixed component, i.e. a reduction of the installed capacity.

The situation is similar in the area of heat consumption for the preparation of hot water. For other years, consumption and cost indicators are shown in the following table.

Table 1 Heat consumption for Hot water preparation

Year	Heat consumption (kWh per year)	Unit cost (€/kWh)	Total cost (€ per year)
2017	157286	0.082	12902.9
2018	144837	0.087	12669.6
2019	148826	0.095	14204.1
Yearly average	150496	0.088	13258.9

3.1.2 Electricity consumption

As part of the work, only electricity consumption in common areas was assessed, i.e. in addition to the lighting of common areas, also the consumption of elevators and office area.

The consumption of electricity in other years is at the level of 8000 kWh per year, while the deviations from this value are not significant. In addition to the balanced annual consumption of electricity, the above is also supported by the monthly evaluation of the consumption of common areas by individual places of consumption for the years 2011-2017.

Table 2 Electricity consumption

Year	Heat consumption (kWh per year)	Unit cost (€/kWh)	Total cost (€ per year)
2017	8135	0.174	1415.24
2018	7674	0.181	1391.10
2019	8007	0.189	1515.94
Yearly average	7939	0.182	1440.76

Balanced electricity consumption and knowledge of consumption throughout the year is very important from the point of view of interest in using a renewable source of electricity, for example a PV.

3.1.3 Conclusion

The apartment building currently spends up to 90% of the funds from the assessed points of consumption to provide heat for the central heating and the preparation of hot water.

It is evident that if you are interested in reducing costs, it is necessary to focus primarily on providing heat in an alternative way that will make the operation of heat production cheaper. However, due to the current and expected situation, it is also necessary to focus on cooling, as the demand for it is constantly growing [7-10] .

Table 4 Utilities and costs

Utility	Unit	Amount	Total cost (€ per year)
Electricity	kWh	7938.67	**1440.76**
Heat	kWh	203629.63	**18130.23**
Heat for HW	kWh	150496.03	**13258.87**
Cold water	m^3	7732.33	**1964.46**
Sewerage	m^3	218.00	**249.94**
Total			35044.26

4 Design and implementation of proposed solutions

4.1 Technologies to increase the efficiency of the building's energy economy

4.1.1 Photovoltaic system for electricity production

In the case of using a PV system, there are several legislative options, to be considered as part of the initial discussions. The PV system proposal is for self-consumption of the produced electricity, operating in island mode. Since the electricity produced by one's own source in the building is very difficult to distribute and bill to individual apartments, two variants of the PV system were designed for the assessed building.

PV system for the need of common areas and elevators

Based on the data supplied by the bulding representatives, we created a consumption profile of the apartment building and consumption points intended for electricity supply from the PV source.

For the given consumption profile and total annual electricity consumption, 6 kWp appears to be a suitable installed capacity of the PV source. However, in order to fulfill the condition of not supplying excess electricity to the network, it is necessary to ensure that the PV system does not produce electricity that cannot be used directly in the building. In the case of the installation of a 6 kWp PV system in the optimal configuration (inclination of panels 36° and orientation to the south), this phenomenon occurs in the months of April to August. The total amount of electricity produced is 6,680 kWh per year, a part will either be supplied to the distribution network free of charge or to the battery system.

A PV system with the same capacity placed on the facade of the building produces 4,605 kWh of electricity annually, which is 2,000 kWh less, but there are no surpluses, and the production is more evenly distributed between the months of March and October.

Table 3 Economy of the 8kWp PV system

CAPEX (€)	11 550.00
Annual energy savings (kWh per year)	6 140.00
Annual energy savings (%)	77.34
Annual savings (€)	1 114.55
Operating life (years)	25.00
Payback period (years)	10.36
Discounted payback period (years)	11.73
NPV (€)	13 412.07
IRR (%)	8.90

A compromise to the above-mentioned systems is a PV system with an installed capacity of 8 kWp located on the southeast facade of the building. With an investment of 11.5 thousand €, the return of the system is at the level of 12 years, with a system lifetime of at least 25 years.

PV system for the need of common areas, elevators, and a heat pump

In the case of using a heat pump to provide heat for preparing hot water and supporting heating, which is mentioned next, it is advisable to install a PV system with an output of 30 kWp on the facade of the building. In this way, the consumption of produced electricity is ensured by the heat pump itself, in case of sufficient heat accumulation, the electricity will be redirected to the current consumption of common areas, or to accumulators for later use.

In the long run, the economics of operating the system is similar to the previous variant in the length of the payback period at the level of more than 11 years, with a difference in the investment and savings achieved after the investment is paid off.

The PV system can be installed in two fields on the southeast facade, the dimensions of one field are 15.3 m in height and 5 m in width. The total number of PV panels is 2 x 45, placed on the facade structure.

Table 4 Economy of the 30kWp PV system

CAPEX (€)	43 347.37
Annual energy savings (kWh per year)	24 000.00
Annual energy savings (%)	66.78
Annual savings (€)	4 356.56
Operating life (years)	25.00
Payback period (years)	9.95
Discounted payback period (years)	11.21
NPV (€)	54 224.23
IRR (%)	9.37

4.1.2 Heat Pump

Currently, the valid legislation does not allow the installation of an own heat source completely replacing supply from central system by disconnecting it. However, it is possible to use a renewable energy source as an additional source of heat to the existing system. Such a source of heat can be a heat pump using waste heat from the building's sewage, i.e. directly from the sewage system [6] .

Heat pump for preparation of hot water

In the case of using the mentioned technology only to provide heat for hot water preparation, the economic parameters of the design are shown in the following table.

Table 5 Economy of heat pump for preparation of hot water

CAPEX (€)	142 121.00
Annual energy savings (kWh per year)	148 825.56
Annual energy savings (%)	100.00
Annual savings (€)	9 797.68
Operating life (years)	25.00
Payback period (years)	14.51
Discounted payback period (years)	17.31
NPV (€)	77 312.30
IRR (%)	5.52

Heat pump for preparation of hot water and support of heating

The heat pump can also use waste heat from the ventilation shafts of the building, in addition to utilization of heat from sewage system. By using a combination of both technologies, it is possible to provide heat for hot water preparation and to support heating. Despite the higher investment, the use of an additional heat source has the effect of reducing the investment payback period to less than 16 years.

Table 6 Economy of heat pump for preparation of hot water and heating

CAPEX (€)	190 033.00
Annual energy savings (kWh/year)	227 977.89
Annual energy savings (%)	153.18
Annual savings (€)	14 501.18
Operating life (years)	25.00
Payback period (years)	13.10
Discounted payback period (years)	15.35
NPV (€)	134 742.03
IRR (%)	6.47

From the above, it follows that if you are interested in the use of technology utilizing waste heat, it is more advantageous to invest in technology combining the use of waste heat from the building's sewage system and waste heat from ventilation shafts.

4.1.3 Renewal of the insulation of the building

The existing insulation of the apartment building, which was installed in 2003, no longer meets current technical standards. At the same time, degradation of the material is noticeable in places, where the insulation loses its effectiveness and heat leaks occur. This measure has the potential to reduce the need for heat by 15-20 % compared to the current state, however, the exact data can only be given after the preparation of a thermal technical assessment, therefore, for the purposes of calculations, a lower limit of -15% is being considered for the time being.

Table 7 Economy of the insulation system

CAPEX (€)	457 145.27
Annual energy savings (kWh per year)	30 544.44
Annual energy savings (%)	15.00
Annual savings (€)	9 797.68
Operating life (years)	25.00
Payback period (years)	46.66
Discounted payback period (years)	>100
NPV (€)	-237 711.97
IRR (%)	-264.16

4.2 Technologies to increase the comfort of apartment building users

In addition to the need for heat and electricity, there is need for cooling, or reduction of overheating of apartments in the summer. Lengthening of the warm seasons and the increase in average air temperature cause an increase in the demand for cooling technologies.

The most common solution are air conditioning units, which apartment owners usually install themselves, or supplier. The disadvantage of separate air conditioning units is, in addition to endangering the maximum reserved capacity of the building by constantly increasing electricity consumption, it also worsens the internal environment of the building and apartments by drying out air and restricting ventilation. Another problem is installation of outdoor units on existing thermal insulation of the building, which causes additional technical problems.

4.2.1 External window shading

When ensuring thermal comfort in apartments, first of all, it is important to prevent overheating of apartments by suitable shading of windows. In this way, it is possible to significantly limit the supply of heat to apartments and reduce the amount of heat entering the building from solar radiation.

High-quality window shading can significantly influence internal temperature and thus also the quality of the environment. In panel apartment buildings, it is standard to use only internal shading, a certain type of internal blinds or blinds. Although they are cheaper than external shades, they have their disadvantages. A lower price is usually reflected in the quality. Common types of interior blinds contain fragile, breakable slats, but also plastic components such as chains or control rods, which degrade over time in the sun and need to be replaced. At the same time, internal blinds allow up to 36 % of solar energy into the room when fully closed, and the incoming solar radiation also paradoxically turns them into an internal heating element and thus contributes to overheating of the building. In contrast, high-quality external blinds can retain 85% to 95% of solar energy even before entering the building. In summer, at high outside temperatures, especially when the window is oriented to the south and west, a reduction of the internal temperature by up to 10 °C can be achieved compared to interior blinds.

High-quality window shading can reduce up to almost 36 MWh of heat per year. Of course, solar gains decrease especially in summer months when it is necessary to prevent overheating of living spaces. In summer months, proper shading can reduce up to 23 MWh of heat in apartments. This represents approximately 0.5 kW of "cooling", or of cooling power per housing unit just by properly shading the windows. The price of Z90 mechanical aluminum external blinds, which are optimal for this type of installation (Z-shaped aluminum slats better withstand adverse conditions such as strong wind and rain), ranges from €150 to €400, depending on the size of window. The total price of the installation for the building is €43,000. However, based on the above data, we recommend installing external blinds only on the south, west and east sides of the apartment building, as the north side does not require cooling in practice.

4.2.2 Active cooling of living spaces

In the case of an apartment building with apartments in long-term use, the installation of wall cooling is problematic due to the existing facilities and equipment of the apartments. Therefore, the presented solution is system of cooling ceilings. In the calculations, a cooling capacity of 1 kW per 1 apartment is considered. The optimal cooling capacity for one residential unit is at least 3 kW, but the considered capacity is related to the technological possibilities of the proposed heat pumps so that the installation of additional cooling technology is not necessary. The system designed in this way can cool living spaces by a maximum of 5°C. The economy of the proposed solution is shown in the following table.

Table 8 Economy of cooling system

CAPEX (€)	249 290.00
Annual cooling capacity (kWh per year)	40 000.00
Annual energy consumption (kWh per year)	54 465.00
Operating life (years)	25.00

With the mentioned technology, it is necessary to keep in mind that it is not primarily a measure to increase the energy efficiency of the apartment building, but that its purpose is to increase user comfort. Therefore, the return on such an investment cannot be calculated, also due to the non-existent cooling system at the moment.

4.2.3 Green roof

A green roof has many advantages on an economic, ecological, but also social level. It retains excessive rainwater, cleans the air, lowers ambient temperature, can regulate the internal temperature in immediate surroundings, saves energy and at the same time supports biodiversity in the city. Green roofs are part of sustainable architecture, which focuses on improving the quality of life in cities and improving the air and overall climate. The main advantages of a green roof include:

- High-quality water retention measure - Green roof can absorb rainwater with the help of plants, substrate and drainage layer. Part of the absorbed water is used to irrigate the plants, part evaporates and the rest is purified by passing through all layers of the green roof. This process reduces and delays the discharge of rainwater into sewers, thereby helping to stabilize the level of stormwater, reducing the load on sewers, and also reducing the risk of flooding.
- Cleans the air - Plants contained in green roof filter solid particles from the air and convert CO_2 into oxygen, thus contributing to cleaning the surrounding air.
- Lowers temperature of surroundings – A high-quality vegetation cover can regulate the temperature immediately below it but also in its surroundings. Plants absorb sunlight, 50% is absorbed and 30% is reflected, naturally helping to create a cooler and more pleasant climate. Studies focusing on green roof research have shown that this measure can reduce roof temperature by up to 10°C in summer months and temperature of living spaces can be lower by 3°C. Adequate reflection of sunlight also lowers the ambient temperature.
- Reduces ambient noise from outside and inside - Green roof serves as a sound barrier, absorbs sound and thus provides a quieter environment inside and outside the building.
- Increases biodiversity - Soil, herbs, grasses or host plants that are part of a green roof support the habitat of birds, butterflies and insects, which is a great benefit especially in an urban environment that is mainly concrete and asphalt.
- Extends the life of the roof - A green roof protects roof material from external influences such as sun, rain, wind and temperature fluctuations, thus doubling or tripling the life of the roof.
- Creates a fireproof layer - Plants naturally contain a lot of moisture. A green roof creates a natural fireproof layer on the building.

- Increases the efficiency of photovoltaic panels - Green roof reduces temperature on the roof. Thanks to this, the efficiency of the PV panels is about 3% higher, which reduces the total cost of purchasing electricity.

Table 9 Economy of the green roof

CAPEX (€)	18 791.00
Annual energy savings (%)	30
Operating life (years)	25.00

5 Conclusion

In order for the economy of an apartment building to function effectively, it is necessary to take it as a whole and harmonize all its technical, technological and construction parts with their use, that is, with the behavior of its inhabitants. Also, on the basis of consultations with the building representatives, we proposed a solution combining the aforementioned technologies into a complex proposal optimized in terms of the client's requirements and the possibilities of individual technologies.

From the point of view of energy production to support the thermal and electrical management of the building, we propose installing a heat pump using heat from the waste sewer, a heat pump using heat from the ventilation shaft and a photovoltaic system on the building facade. It is up to the building owners to consider the replacement of the building's insulation due to the economic evaluation.

In order to increase the user comfort of residents, we suggest installation of external blinds to shade solar radiation on the south, east and west sides of the building, reverse operation of the above-mentioned heat pump to also serve for cooling, distribution of cold to the apartments and the Uponor ceiling cooling system and a green roof to prevent overheating roofs in the summer, in addition to retention of excess rainwater and moisture.

5.1 Evaluation of technology to increase the efficiency of energy efficiency of the buildng

The following table shows the energy parameters of the proposed solution, with the energy produced in the indicated values, the remaining energy will need to be purchased from distribution networks. The heat pump is installed to cover the year-round preparation of hot water and at the same time to support the heating. However, this means that the total electricity consumption of the building will increase. Therefore, a photovoltaic system is proposed, which will cover a significant part of the electricity consumption for hot water preparation and building’s internal consumption for lighting, elevators and common areas.

Table 10 Energy parameters of the proposed solution

Installed capacity (kW)	*PV*	*45*
	Heat pump for hot water production	20
	Heat pump for support of heating	30
Energy production (kWh/year)	Electricity	40 763
	Heat for hot water production	148 826
	Heating	79 152
Energy consumption (kWh/year)	Electricity	27 449
	Heat for hot water production	3 069
	Heating	121 856

The following table shows the economy of the building if only technologies to increase the energy efficiency were applied to the current state. The total opex of the building will be reduced from the current €42 556 to €24 936. This represents annual savings of almost €18 000.

Table 11 Economy of the proposed solution

OPEX for current status (€/year)	42 556
CAPEX (€)	271 347
OPEX of proposed solution (€/year)	5 083
Utilities (€/year)	19 567
Total OPEX (€/year)	24 651
Annual savings (€/year)	**17 905**

If we assume a 2 % level of the discount rate, which is a common value for projects of this type, the return on the investment is at the level of 19 years and the investment has a positive return of over €113,000 at the end of its useful life. This value represents the net earnings of residents. The stated return exceeds standard and acceptable return values even in energy projects. All projected costs are calculated at current energy prices. However, as could be seen above from the tables and graphs in chapter 1, heat prices have increased 5-7 times over the last 25 years. If we assume a similar development for the next 25 years, the payback period and also the total yield from the installed technology will be relatively shortened.

One of the main factors in the renovation of an apartment building should be the reduction of emissions. The proposed measures will significantly reduce the annual emission production of the apartment building and contribute positively to the long-term goals of the environmental policy and the improvement of the environment. After implementation of the proposed solution, there should be a reduction in emissions compared to the current values by 27 % (solid pollutants) and 63 % (CO and CO_2).

5.2 Technologies to increase the comfort of residents

When summarizing the parameters of technologies for comfort increase, we did not calculate the return of the project, as it is an investment in above standard technology, or technologies to increase the user comfort of residents. These measures represent a net burden and increase in consumption from an energy and economic point of view. The investment includes the installation of external mechanical shading on the south, west and east sides of the building, application of the reverse operation of the heat pump so that it can be used for cooling, cold distribution to the apartment units, cooling ceiling panels for apartments and the installation of a green roof.

However, it should be noted that the need for cooling will already be a standard need soon. In recent years, we can observe the growing trend of installation of air conditioners in individual households. Such a solution, when each household deals with cooling independently, is very disadvantageous from an environmental (high electricity consumption = high emissions), aesthetic (installation of units on the facade of the house) and economic (high consumption = high costs) point of view, and therefore it is proposed to apply a common solution.

Since the measure to increase comfort is a net burden from the energy point of view, it also represents a contribution to the increase in emissions compared to the current state, 0.35% (CO) and 8.36% (solid pollutants).

On the contrary, a green roof contributes to reduction in the negative consequences of a warming climate in a natural way. With the correct composition of the individual layers of the green roof, it is possible to achieve a stable roof temperature (cooling of the roof in the summer months by up to 10°C), reduction of solar radiation degrading the top layer of the roof covering, reduction of the amount of rainwater drained into the sewer system and increase in the comfort of the residents of the upper floor. as there will be no overheating of their apartments in the summer.

5.3 Complex solution

It is logical that by combining the above-mentioned solutions, the investment in the ecological renovation of the building will be not profitable from economic point of view. Nevertheless, user comfort or the environmental benefit of the renovation should also be considered, not just the economics of the project itself. Again, it is necessary to remind that the economy is calculated at current energy prices, which have had a steep growth trend for the last 25 years and tremendous increase during last year, which means that with increasing prices, the project has an even higher value, as total revenues increase and the payback period shortens.

Table 12 Energy parameters of the complex solution

Installed capacity (kW)	PV	45
	Heat pump for hot water production	20
	Heat pump for support of heating	30
	Cooling	50
Energy production (kWh/year)	Electricity	40 763
	Heat for hot water production	148 826
	Heating	79 152
	Cooling	40 000
Energy consumption (kWh/year)	Electricity	32 914
	Heat for hot water production	3 069
	Heating	121 856

Despite the increase in the investment and operating costs of the building by technologies intended only to increase the comfort of residents, these measures represent a positive benefit not only from the user, energy and environmental point of view, but also from the economic point of view. Compared to current costs, OPEX will be reduced by more than €14 000 per year.

Table 13 Economy of the complex solution

OPEX for current status (€/year)	40 990
CAPEX (€)	553 038
OPEX of proposed solution (€/year)	6 387
Utilities (€/year)	20 602
Total OPEX (€/year)	26 989
Annual savings (€/year)	14 001

Table 14 Energy and emmission balance

Item	After renovation	Reduction (%)
Heat consumption (kWh per year)	124 925	65
Electricity consumption (kWh per year)	31 402	-280
CO production (t per year)	0,259	63
Solid pollutants (t per year)	0,009	21
Annual CO_2 production (t per year)	75,827	62

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New Generation of Refractories for Rotary Cement Kiln

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Keywords: application in the cement industry, cement rotary kiln, lining design, refractories, wear lining

Abstract : The article describes a rotary cement kiln and its process, discusses primary and secondary fuels and presented stresses on the refractory lining. The authors present various wear and lining concepts. In the contribution are summarized practical development applied to these aggregates. Optimum lining performance throughout the kiln can be achieved by appropriate refractory selection. Finally, this article highlights some types of newly developed refractory materials for the basic lining in modern cement rotary kilns.

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1 Introduction

All thermal industrial plants operating at temperature higher than 1000°C, including cement industry plants, needed refractory linings for thermal insulation and in order to maintain resist the necessary process temperatures.

A comparison of industries (Figure 1) shows, that the iron and steel industry is main consumer of refractory materials, followed in second place by the energy and petrochemical industry, further follows non-ferrous metals and cement industry which, though smaller (8%), still requires independent research and development in its specific field of refractory materials [1,2].

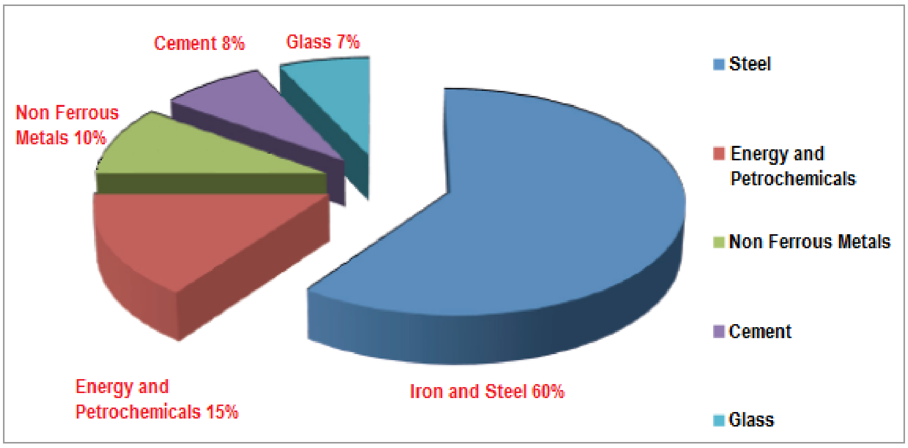

Figure 1 Worldwide consumption of refractories [2]

This is because refractory linings are subject to a wide range of destructive influences trough the mechanical Dynamics of cement rotary kiln, the chemistry of the cement clinker process and the types fuels used (Figure 2). These influences include [1]:

- mechanical loads due to deformation of the kiln shell and temperature variations,
- chemical loads caused by infiltration of clinker melt, alkali salts and local reducing conditions,
- thermal loads due to overheating.

The intensity of these stresses varies according to the operating condition and kiln sections. There is no „universal brick“ suitable for all cases, but a range of refractory materials with different properties to ensure appropriate zone lining [1].

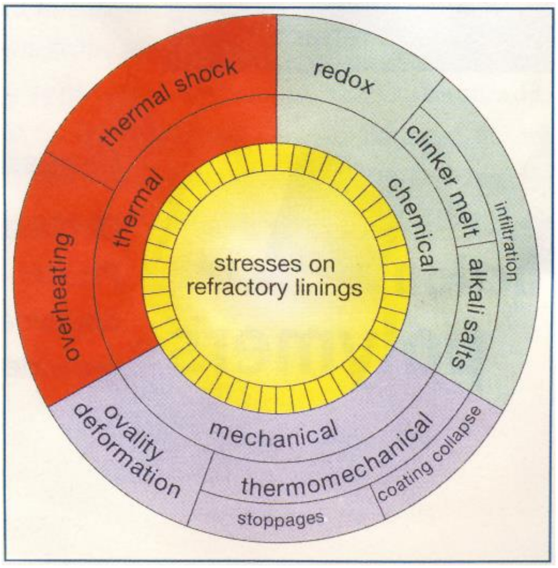

Figure 2 Stresses on refractory linings [1]

2 The rotary kiln and its process

The development and bulk production of modern Portland cement is directly linked to the rotary kiln and its ongoing technical development.

The first cement rotary kiln started operation in 1899 at a cement plant in Hanover. Its capacity was 80 to 100 t/d. Then rotary kiln technology surged forward. Today, maximum capacity of a cement rotary kiln of 12000 t/d cannot be obtained with other kiln units.

The develop of the burning processes is particularly characterised by reduction in specific energy demand and increases in the specific clinker throughput (Table 1), especially due to the switch from wet and dry rotary kilns to the Lepol kiln and suspension pre-heater kiln.

However the thermal cross-sectional load rose sharply at the time, leading to increase refractory wear within the burning zone, especially in pre-heater kilns and thus to frequent kiln stops.

Thermal relief of refractory material was obtained in the seventies by introduction of kilns with pre-calciners. Secondary firing in the pre-heater system decarbonates the raw material by up to 90% before enters the rotary kiln, where sintering during the melting phases of the kiln feed and formation of the clinker minerals take place [1].

As a consequence of these changes, rotary kilns were shortened from e.g.200-m wet kilns to 40-m pre-calciner kilns with equal capacity.

The specific throughput, measured on the basis of specific kiln volume load, rose from 0.5 to 5 t/m^3. This was achieved by, among other things, increasing the revolutions per minute from 1.3 to 3.5.

The diameter- length ratio of the modern kiln with cyclone and great pre-heater is 10:17. This kiln runs on only two tyre station. As there is no longer a third tyre, the bearing of the rotary kiln now is statically determined and thus kiln distortion, which frequently leads to the destruction of refractory lining where there are three and more tyres, has been avoided [1].

”Rotary Kiln Tyre“ is also called the rolling ring. Its function is to transfer all the gravity of cylinder (including the gravity of refractory bricks, internal devices and materials) to the supporting roller rotate smoothly on the supporting roller. The belt should have sufficient strength and durability. At the same time, on rotary kiln is a part that strengthens the radial rigidity of cylinder and should sufficient rigidity [3].

Table 1 Chronology of dimension and specific loads for various rotary kiln [1]

	Length (l)/m	Ø/m	Ø/l	Kiln volume load /t/m^{2}d	Thermal cross sectional load /Gcal/m^{2}s	Specific heat consumption /kcal/kg clinker
Long wet kiln	200	5.6	1:37	0.5	5.9	1400
Long dry kiln	162	5.4	1:30	0.64	5.2	1150
Lepol kiln	74	4.6	1:16	2.0	4.9	800
Suspension preheater kiln	64	4.6	1:14	2.3	4.8	750
Precalciner kiln (traditional)	54	3.8	1:14	4.1	3.2	750
Precalciner kiln (short)	40	4.0	1:10	5.0	2.85	750

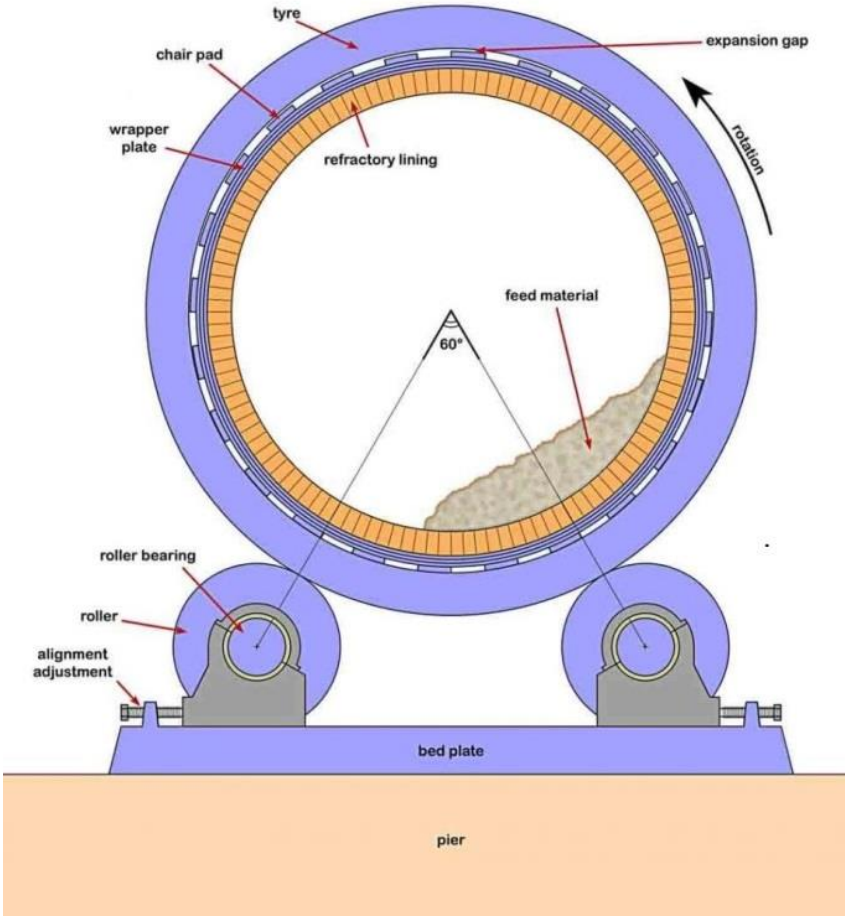

Figure 3 Schematic section drawing of cement kiln [4]

Figure 3 shows schematic section drawing of cement kiln and Figure 4 shows a view of cement kiln with roller station (tyre, rollers).

Figure 4 Cement kiln with roller station [5]

3 Primary and secondary fuels

In modern, waste-fired cement kilns, harmful atmospheric particles in the kiln gases are primarily responsible for the degradation of the refractory lining. The new formation of mineral phases is based on infiltration and chemical interaction with primary mineral phases. This lead to a differentiation of the physical properties towards temperature gradients in the direction of the kiln shell. Sui-table new product developments need to be chemically inert to alkali and sulphur and demonstrate a maximized infiltration resistance. It is self-evident that adequate thermochemical resistance to the cement clinker must be present in each zone of use [6].

As a result of two serious the energy crises 1973/1974 and 1979/1980 there was a radical change in fuel base in the cement industry. From heating oil and natural gas, they switched to less valuable coal and began burning waste materials e.g. tires, plastics and solvents. At the same time, a pre-calcination system was introduced in which decarbonisation occurs outside the rotary kiln. The cement rotary kiln became “waste incinerator”.

This development led to a change on the refractory lining throughout the furnace system [6,7]:

- the burning zone was thermally relieved,
- the low service life of refractory lining caused by thermal overload has been removed.

The refractory industry was confronted with a new challenge. Depending on the type of secondary fuels and their quantity used, not only alkalis, chlorides, sulphates, sulphides and sulphuric oxides, but also heavy metals and trace elements such as lead, cadmium, chrome, cooper, nickel, mercury and selenium were massively introduced into the kiln system (Figure 5) [7,8]. These substances infiltrate and corrode the refractory lining, some right up to the kiln shell. Furthermore, when firing with secondary fuels, local reducing conditions occur due to the carbon monoxide which is released during the de-gasification and delayed combustion of the secondary fuels [1].

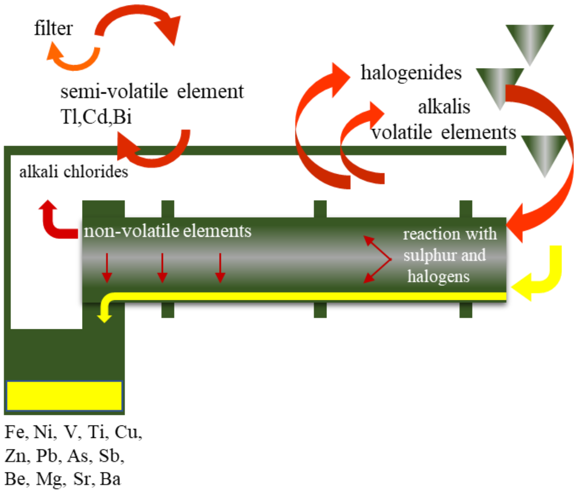

Figure 5 Behaviour and transfer of some basic elements introduced into the cement kiln [7,8]

In the furnace system can be internal and external circulation of these substances, which depending on their volatility, are incorporated (built) either into cement clinker or they become part of the furnace atmosphere and thus create a non-negligible circulatory load, as schematically shown in Figure 5.

The influence of various factors on the wear of the lining of cement rotary kiln is show in Figure 6. These data is the result analyses performed in the past.

4 The burning zone lining

The heart of cement kiln is the burning zone, where the final formation of the clinker phases place at 1450°C with liquid phase sintering. The length of this burning zone in modern pre-calciner kilns is 8-10 times the diameter. Usually, its linings is covered and protected by a coating layer.

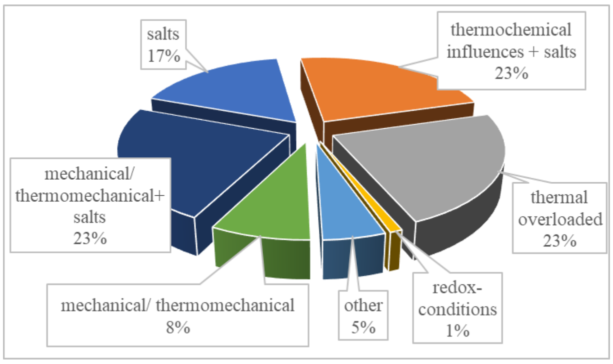

Figure 6 The influence of various factors on the wear of cement rotary kiln lining [7, 8]

The central burning zone is flanked by a coating-free upper and lower transition zone, each twice the diameter in length. Both zones are unprotected and exposed to gas temperatures of 1800°C in the rotary kiln. Therefore, the lifetime of cement burning kiln depends principally on the durability of the burning zone's lining, as it suffers greater wear than the pre-heater zone and cooler zone.

Generally, the durability of a burning zone is between 9 and 12 months, depending on the kiln system and operating conditions, whereas the refractory lining of a pre-heater or cooler zone reaches 12 to 48 months, making it not necessary to repair every section equally frequently.

The historic overview shows, that the rotary kiln process started with the use of fireclay and alumina-rich bricks. These brick grades rendered satisfactory service in small kilns with a low capacity.

The appearance of the Lepol kiln and pre-heater kiln, but also the long wet and dry rotary kiln, necessitated the development of brick grades with higher resistance. This requirement was met with magnesia-chromite bricks with a silicate bond. The special properties of magnesia-chromite bricks with direct bond, which successfully used in the steel and non-ferrous metal industries, were not relevant in the cement industry. Within approximately the same period, ecological concerns such as Cr^{6+} problems became more and more driving force for further development of magnesia-based bricks [1].

At the beginning of the eighties, chrome-free magnesia brick grades containing synthetic spinel ($MgO \cdot Al_2O_3$), hercynite ($FeO \cdot Al_2O_3$) or galaxite ($MnO \cdot Al_2O_3$) as secondary component appeared on the market. The primary function of the additives of the spinel group was to minimise of the magnesia bricks.

Also worth mentioning are burnt dolomite (doloma), which attain good durability results in the central burning zone, given a stable coating. However, in coating-free areas their CaO content react with the kiln gases and leads to the formation of zones of $CaCO_3$, $CaSO_4$ or CaS [1,8]. Furthermore, these bricks possess only low resistance to humidity, which is a disadvantage during storage or kiln stop.

The most important material properties of basic burning zone bricks are listed in Table 2.

Table 2 Main properties of bricks for the basic burning zone [1]

Chemical composition/ %	Magnesia chromite	Magnesia spinel	Magnesia hercynite	Magnesia galaxite	Magnesia zirconia	Dolomite
MgO	81-85	85-89	87-92	90	92-96	38
Al_2O_3	1-3	9-12	4-6	3.6	<0.5	0.4
Cr_2O_3	3-5					
Fe_2O_3	7-9	0.5	3-5	0.8	0.6	1.0
Mn_2O_3				3.6		
CaO	2.5	1	1.5	2	1.3	58
SiO_2	1.5	0.5	0.5	0.7	<0.5	1.0
ZrO_2					2-4	(1.3)
Bulk density/g/cm^3	3.00	3.00	2.90	2.93	2.90	2.85
Open porosity/vol.%	18.0	14.0	18.0	17.0	18.0	16.0
Cold crushing strength/ N/mm^2	55	70	50	90	50	50
Thermal shock resistance	80	100	100	>50	100	>30
Thermal conductivity (at 100°C) W/mK	2.8	2.6	2.6		2.9	2.4

5 Wear and lining concepts

The trend in specific refractory consumption in modern cement burning plant recorded a decrease from 2.2 to 1kg/t since 1955. The best values are 800 g/t in 1980 and 400 g/t clinker to day.

There are several reasons for this: There can be no doubt that refractory industry has continually developed better refractory materials through which the availability and performance of cement kilns has increased. This would not have been possible, however, without the switch from the long wet rotary kiln to pre-calciner kiln.

Current technological know-how has led to a general refractory lining concept for cement burning kilns that used different brick grades and concretes. This represents the state of the art (engineering). The lining of the rotary section consist of fireclay bricks and high-alumina bricks with the addition of SiC in the so called safety zone below 1250°C.

For the following burning zones magnesia-chromite bricks and lately magnesia-hercynite bricks have given excellent results. Magnesia-zirconia or dolomite bricks (doloma) are used less frequently, depending on the particular operating conditions [1,8]. Main properties of bricks for the basic burning zone are listed in Table 2 [1].

Considering the above, we could ask whether the research and development of refractory materials for the cement industry is completed. The answer has to be “no”, for the following reason. An analysis of wear causes clearly shows that 63% of the cases of damage are due to the influence of alkali compounds and sulphur oxides resulting from the combustion of secondary fuels, i.e. waste incineration. This wear cause is followed in importance by wear due to thermal overloading (23%) [1].

Other causes of wear can be neglected owing to the variety of refractory materials available, better process control, and improved kiln design (Figure 6).

Therefore, the main of all research and development activities in cement industry will be the improvement of resistance to in infiltration and corrosion caused by alkalis, salts, and SO_2/SO_3. This affects basic and alumina-rich bricks, unshaped refractories and heat-insulating materials. Here, the requirements concerning fracture toughness and creep behaviour of the materials should not be ignored. In the case of unshaped refractory materials, the development of a basic material possessing properties similar to magnesia-chromite and magnesia-spinel bricks would be interesting, because this would lead to a refractory material which can be installed in the hotter zones of a cement kiln [1].

6 Innovative solutions for rotary kiln lining

The impact of the increasing use of secondary fuels and raw materials on the production of cement up to now is still rising regarding the requirements on the refractory lining of cement kilns.

Additionally, mechanical loads require stringent attention as well. By applying concepts involving the refractory lining as a whole it has become possible to reduce the physical and chemical wear caused by infiltration [1,10]. Still the growing primarily chemical and mechanical load demands intensified developments of new brick generation. This paper present some types of newly developed refractory materials:

- Pleonastic spinel
- Magnesia-spinel
- Chrome-free

6.1 Pleonastic spinel refractory bricks

The production of cement clinker in high performance furnaces is not possible today or in future without development of sophisticated elastic shaped bricks. This can be achieved with the help of so-called elastifier**.** Technically and economically it was proven that they are most suitable for this purpose are spinel minerals. Hercynite and galaxite are referred to in the professional literature as active spinels.

Pleonastic spinel is currently being proposed as the latest alternative to hercynite [11], which, in addition to Fe_2O_3 and Al_2O_3 also contains MgO. It is produced industrially by melting spinel or by sintering a suitable mixture. This product is characterized by better resistance to corrosion by cement clinkers, while the building materials maintains a good ability to create and maintain a protective coating [11].

In Figure 7 is a brick structure showing pleonastic spinel with stabilizing MgO precipitations and in Figure 8 is a view of the coating on magnesium brick containing pleonastic spinel [8, 10].

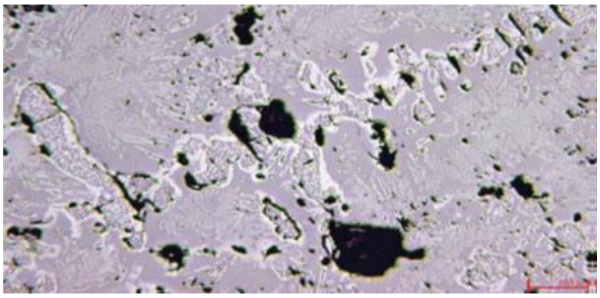

Figure 7 Brick structure showing pleonastic spinel with stabilizing MgO precipitations [8,10]

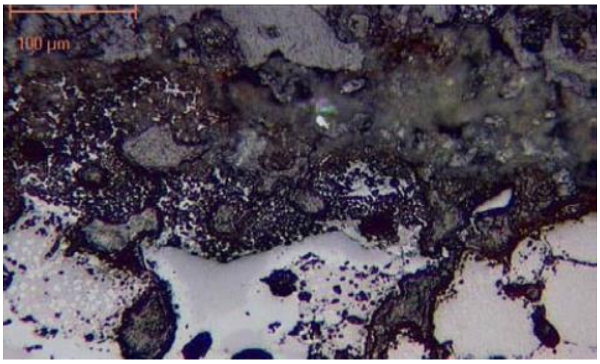

Figure 8 Coating on magnesium brick containing pleonastic spinel [8,10]

As for the practical application of bricks containing pleonastic spinel, the superior performance of this new brick type is shown in two case studies (Figure 9).

Although magnesia spinel bricks and magnesia hercynite bricks currently are standard products for lining cement kiln, their application-oriented properties can be refined so that they also behave excellently even under increasingly severe conditions. By mineralogical conversion a new spinel type is introduced into the brick structure, which best may be described as spinel of pleonastic type.

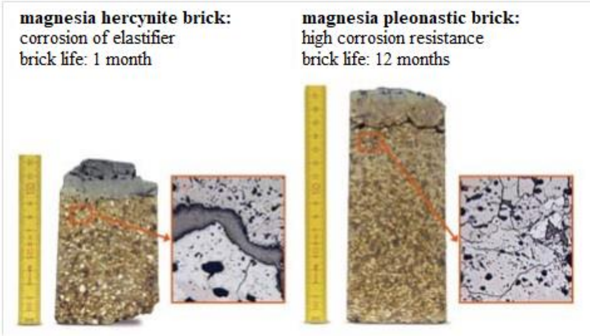

Figure 9 Corrosion of magnesia hercynite and magnesia pleonastic bricks [8,10]

The bricks which take advantage of this specially designed spinel show an extremely good resistance to attack of cement clinker, a superior thermal shock resistance and a coating behaviour which is comparable to the one of the now magnesia chromite bricks. The structural flexibility corresponds to that of the well – established magnesia spinel bricks. They can therefore be used not only in the sintering zones, but also in the upper transition zones of cement kiln in case of increased thermal loads. Owing to their low porosity, the bricks are also characterized by an increased resistance to alkali attack [10].

6.2 Refractory magnesia-spinel bricks

Recently, lining bricks in burning zone of cement rotary kilns have been severely damaged by clinker melt attack and thermal shock because they are exposed to unstable coating conditions due to increasing use as fuels and raw materials.

The responding to varying operational conditions and increasing mechanical stress led to the development a magnesia – spinel brick that has good coating adhesion and high resistance and spalling. The developed brick demonstrated superior properties, compared of another type bricks used in cement rotary kilns.

Zirconia-added magnesia –spinel bricks composed mainly of magnesia (MgO) and spinel ($MgO.Al_2O_3$) are extensively used in burning zone of cement rotary kilns. This is because they can have both good coating adhesion and high corrosion resistance to the clinker melt while maintaining their high spalling resistance. The wear of the bricks has increased due to unstable coating conditions arising from the increasing use of alternative fuels and raw materials. In order to improve the performance, researchers focused on:

- coating adherability,
- corrosion resistance,
- spalling resistance.

These are properties of the bricks required for harsh environments in burning zone [12]. Figure 10 shows a view of the interior of cement kiln in the past (25 years ago) and present immediately after shutdown [12].

Figure 10 Appearance of inside of past (25 years ago) and present cement kilns after shutdown [12]

6.3 New chrome refractory bricks

Chrome free bricks are largely used in present time in cement rotary kilns. However, the life of these bricks has been shortened remarkably, especially at burning zone, due to the increased use of wastes as raw material and fuel [13].

Cement rotary kilns does a major contribution to environmental preservation because of its feature of processing a large amount of waste and recycling them safely. The amount of waste such as scrap tire, paper manufacturing industry, coal ash, from electric power–related industry, plastic from food industry, waste oil, sludge from petroleum industry, and other waste is increasing remarkably. At present, the amount of waste in the advanced countries in the world is more than 450 kg per ton, and it is going to increase with the years. Associated with increase and diversity in the waste disposal, which contain alkalises, chloride, sulphur and other chemicals, the coating in the burning zone has been instable, turning the burning zone of the rotary kilns severe, whereby the melting and other damages of lining bricks is proceeding at an accelerating rate [13].

The properties needed for the brick for the burning zone under those severe conditions is:

- high coating adhesion performance,
- high corrosion resistance,
- high stress relaxation function.

Although magnesia-chromia bricks have some of the above properties, they have some environmental problems, especially after use. High performance chrome free bricks have been desired these days.

Chrome free bricks which exhibit excellent resistance to corrosion, penetration, and thermal spalling. The bricks are mainly made from magnesia and/or a magnesia spinel material and comprise 1 to 10wt % titania and 1 to 15wt% alumina. They may contain 0.5 to 10wt% iron oxide. Further, they may contain at least one material of the group consisting of 1 to 20 wt% one of oxide materials except for iron oxide [14].

The result showed that with addition of TiO_2 reactions between MgO-TiO_2 has reinforced the microstructure of brick. Meanwhile, TiO_2 improved all properties as well as the coating ability on corrosion resistance of the bricks that exhibit good-thermal stability and excellent chemical resistance against clinker raw meal. As a result, this brick has qualities needed in the burning (hot) zone of rotary cement kiln [15].

In recent years, the performance of a ferromagnesium (ferrous) aluminum chromium-refractory brick made by special calcinations using synthetic ferrous spinel as an elastic agent and sintered magnesium oxide containing iron oxide as raw materials has attracted attention entitled ”chrome-free alkaline bricks”. The chemical composition of chrome ore, magnesia-alumina spinel, and ferrous spinel as elastic agents are show in the Table 3 [16].

Table 3 The chemical composition of chrome ore, magnesia-alumina spinel and ferrous spinel [16]

Chemical composition	Chrome ore	Al-Mg Spinel	Ferrous spinel
SiO_2	0.5~2	<0.5	<2.0
Al_2O_3	10~25	67	35~60
Fe_2O_3	14~28	<0.5	20~30
Cr_2O_3	30~48	-	-
MgO	12~20	32	20~30
CaO	<0.8	<0.5	<0.5

6.3.1 Chemical properties of chrome-free alkaline refractory bricks

The chemical composition of ferrous-spinel made of ferrous-spinel as on elastic agent in the MgO-Al_2O_3-Fe_2O_3 system differs greatly from that of magnesium-aluminum spinel, but close to the composition of chromium ore. In the brick production process, Al_2O_3 and MgO or FeO/Fe_2O_3 are easier to replace Cr_2O_3, so the refractory brick made do not contain Cr_2O_3.

Ferrous spinel, magnesia spinel, and C_2S, which are made of ferrous spinel and sintered magnesia containing iron oxide are easy to interact with the kiln material to produce high-viscosity calcium ferrite and calcium aluminate compound improves the performance of hanging kiln skins, surpassing spinel and magnesia-chrome bricks [16].

Figure 11 shows status kiln skin sticking to ferrous magnesia and alumina spinel refractory bricks [16].

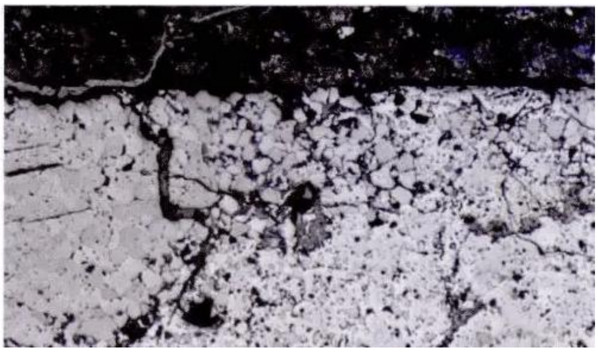

Figure 11 Status kiln skin sticking to ferrous magnesia and alumina spinel refractory brick [16]

6.3.2 Physical properties of chrome-free alkaline refractory brick

The ferrous alumina spinel bricks have excellent elasticity and thermal shock resistance, a reduction in creep stress, and magnesium and chromium compared with brick, it has better thermo-mechanical properties.

Under the appropriate fire resistance, the compressive strength is about 20% higher. Porosity is only 13-15%, which is about 3-4% lower than that of magnesia-chrome brick. Without affecting other properties, the melt penetration resistance is increased by about 25% (Figure 11) [16].

Figure 12 shows the dependence of physical properties of magnesium-chromium bricks and magnesium, ferrous alumina spinel on related performance where is: SSI- Stress sensitivity index [MPa], CCS – Cold press strength [MPa].

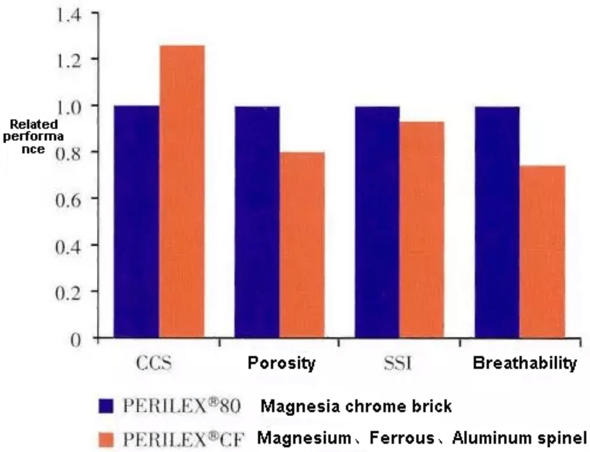

Figure 12 The depence of physical properties bricks on related performance [16]

7 Conclusion

Pleonastic spinel, magnesia spinel and chrome free bricks with excellent high temperature characteristic and improved resistance against chemical corrosion are available now to match the requirements for the basic lining in modern cement rotary kilns. Optimum lining performance throughout the kiln can be achieved by appropriate refractory selection. Depending on kiln conditions, particular zones within the kiln require different basic refractories.

The pleonastic-spinel lining in the burning zone is characterized by extremely good resistance to attack by melt clinker, a excellent resistant to thermal shocks, and coating, which is comparable to the one of the now magnesia-chromite bricks.

The lining in the burning zone, which is made of magnesia-spinel bricks is characterized by coating adhesion, corrosion resistance and resistance to spalling.

The lining in the burning zone, which is made of chrome-free bricks is characterized by high coating performance, high corrosion resistance and high stress relaxation function.

Development of refractory materials for cement kilns, especially in the burning zone will be continue also in the future as more and more waste is used to a replace fuel and raw materials, which requires the development of even better quality refractory materials.

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