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# RESEARCH ON INCRUSTATION IN A MODEL EVAPORATIVE COOLER

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The paper presents research on scale formation performed in a laboratory model of an evaporative cooler. Such type heat exchangers are often applied in industrial cooling systems. As a heat carrier they usually use raw water, which despite its numerous advantages is also a source of many problems like corrosion and incrustation. The elaborated model makes possible to perform qualitative and quantitative testing of crystalline deposits that form on heating surfaces. The following tests performed with the application of the mentioned cooler model have been presented in the paper:
1. phase crystallization of calcium carbonate,
2. ammonium sulfate effect on incrustation in a model heal exchanger.

Diffractometric tests have shown differences in phase composition of calcium carbonate deposits, which have formed at different temperatures and in the presence of ammonium sulfate. At $40^0$C calcium carbonate has formed as anhydrous calcite and monohydrate while at 55-$60^0$C additionally as aragonite. An addition of ammonium sulfate has inhibited scale accretion and even caused its insignificant dissolution.

*Key words: cooling water, scale water, treatment, ammonium salts*

## INTRODUCTION

A continuous social and economic developments involve ever-increasing demand for water of adequate quality. Meeting of the demand requires many actions of various kinds and in that number shutdowns of water-based cooling systems that are applied in many industry branches.

In recirculating cooling systems the cooling effect is mainly obtained by evaporation of a part of water (high heat of evaporation). It is the reason why in such systems a fraction of the water volume gets consumed as compared to once-through cooling systems. However, water evaporation brings about its condensation, which causes exceeding the solubility product, especially of the main component of raw

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water i.e. calcium carbonate, which in turn results in the precipitation of deposits called scale. There are also other problems that occur in water-based systems such as corrosion of construction materials, sludge formation, and biological fouling (Kowal, 1980). The presence of deposits on heat exchanger surfaces is of significant effect as it impedes heat flow and then the installations operate at a reduced efficiency.

Calcium carbonate deposits can form for the following reasons:

- susceptibility to deposit formation under the influence of temperature changes, which has an effect on the $CaCO_3$ solubility,
- changes in the solution pH, which disturbs carbonate-calcium equilibrium and causes $CaCO_3$ precipitation or its dissolution.

Calcium carbonate can crystallize in three forms: calcite, aragonite and vaterite. Conditions for the formation of individual phases have been discussed in many publications (Xu, et al. 1999; Turner, et al. 1998; Wray and Daniels, 1957). The present paper presents a research on calcium carbonate formation in a laboratory model of a spray-evaporative cooler.

## QUALITY OF COOLING WATER

The basic requirement for cooling water is the so-called stability (Gomółkowie, 1994). Water stability can be defined as property that there is neither precipitation nor dissolution of calcium carbonate. In the case of spray-evaporative condensers it is practically impossible to maintain the stability as the cooling water temperature is about $30^oC$ while the temperature of hot coil pipes in extreme cases can reach even $50–60^oC$. In such a case the conditions for the formation of dense scale deposits occur, especially that water gets condensed as a result of partial evaporation.

Considering various anti-scaling methods that are in use, two directions can be distinguished:

- introduction of supplementary water with most of the scale-generating pollutants removed,
- treatment of the circulating water by the addition of incrustation inhibitors.

Sometimes both approaches are jointly applied - preliminary treatment at first and then stabilization to inhibit scale formation in the course of water condensation. The application of inhibitors is simple and efficient as compared to other methods commonly used for the protection of industrial water-based systems. Modern inhibitor programs for cooling water treatment can be classified into three extensive groups (Ascolese, 998):

- acid method where pH of water is maintained between $6.0 \div 6.7$,
- neutral programs at the water pH of $6.8 \div 7.8$,
- alkaline programs when the water pH is $7.8 \div 9.0$.

Working with acid or neutral pH usually consists in maintaining the pH at an adequate level with the use of acid - usually HCl or $H_2SO_4$ - which is called acid grafting. Alkaline programs do not need pH correction but their disadvantage is that there is a hazard of massive deposit formation, mainly of carbonates and that is why it is necessary to maintain low coefficient of water condensation, which increases water treatment costs.

Acid action is an efficient way to inhibit scaling and remove already-formed deposits but there is a risk of its overdosing and causing corrosive damage to the installation. Additionally, for economical reasons, acid grafting is not recommended when carbonate hardness of water exceeds 100 mg $CaCO_3/dm^3$ (Gomółkowie, 994).

Instead of acid, it is suggested to apply a salt of weak base (ammonium) and strong acid (hydrochloric, sulfuric). The salt hydrolyzes and safely acidifies the environment (Zagórski, et al. 1978):

$$NH_4^+ + H_2O = NH_4OH + H^+$$

The equilibrium constant is ca. $2 \cdot 10^{-5}$, so the cooling water pH does not drop below 6 when such salt is added. A total lack of prevention can lead to the formation of thick scale deposits, which dramatically decreases heat exchange efficiency (Fig. 1).

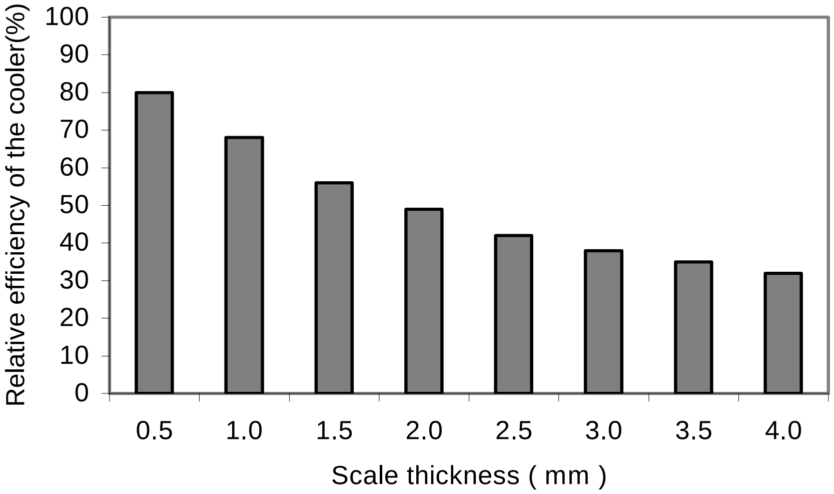

Fig. 1. Efficiency of an evaporative cooler vs. scale thickness

## INDUSTRIAL STANDARD OF AMMONIA EVAPORATIVE CONDENSERS

Exchangers of the discussed type are often applied in the industry and especially in cold stores and plants of the fruit-and-vegetable processing branch. Operation of an evaporative condenser consists in pumping refrigerant vapor (ammonia) with a compressor to the cooling system. The vapor gets condensed under constant pressure and temperature. Heat gets absorbed by air and water at the external side of pipes. Application of the both media is thermodynamically and economically justified, as they are easily available. For air there is practically no limit of availability although from the thermodynamic point of view water is much better applicable. However, water resources are limited and water treatment costs should also be considered, both of which make its availability worse than it is in the case of air.

Figure 2 presents a diagram of a typical spray-evaporative industrial condenser (Zalewski, 1998). Coils made of smooth pipes make its principal part. Cooled ammonia flows in the pipes in the downward direction. A spray system is installed above the coils to uniformly distribute water over the coil pipes. A catch-drop composed of adequately shaped elements meant to catch water drops carried with the air stream is mounted above the spray system. Outer surface of coils is sprayed with water that gravitationally flows down the warm pipes. Water evaporates into the air stream and gives up the heat received through the pipe walls form the condensing ammonia.

Cooling water works in a recirculating system. It is fed from a water tank and transferred by means of pumps to the spray system. A constant addition of fresh makeup water is required because of the water bulk losses resulting from its evaporation, being carried away by the air stream, leaks, and also from sludge removal performed to maintain optimal condensation level of water.

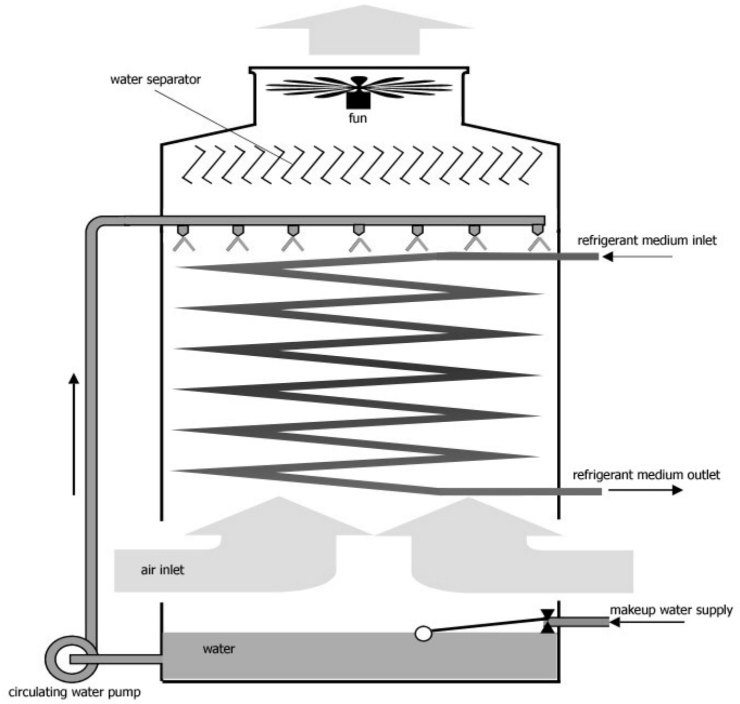

Fig. 2. Diagram of an industrial evaporative cooler

## TESTS ON SCALE FORMATION PERFORMED IN A MODEL HEAT EXCHANGER

A model of a heat exchanger of the spray-evaporative type has been elaborated for the testing purposes. The model makes possible to perform simulation of processes that run in an industrial installation at the water-air side, where conditions for scale formation occur. Figure 3 presents a diagram of the model. The model consists of:

1. a tank of circulating water with a valve for its partial drain to perform sludge removal,
2. a set of steel pipes that serve as a coil with water inside and a thermostat connected to the water circulation system,
3. perforated troughs that distribute water at the exchanger top to uniformly spray the pipes,
4. water pump that makes water circulating,
5. air chamber to realize free airflow from the bottom of the pipes upwards,
6. drain valve to control condensation level of recirculating water,
7. inlet for air stream directed counter-current to the gravitationally flowing water.

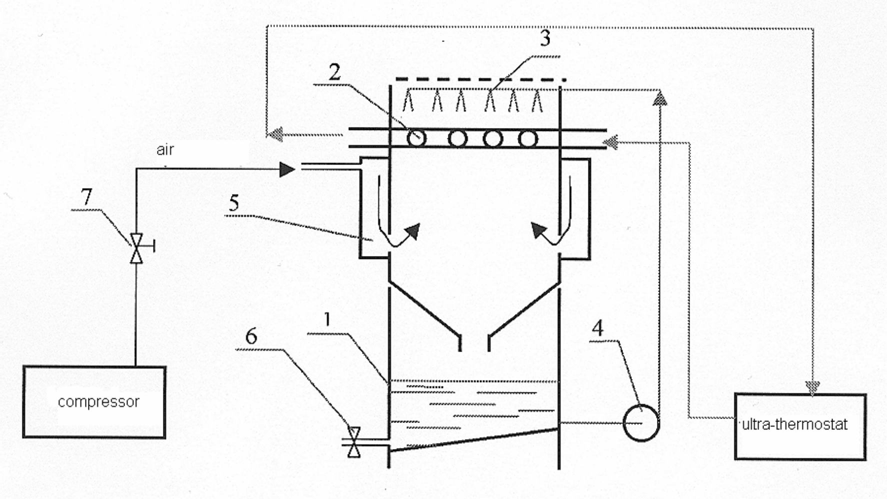

Fig. 3. Model of a spray-evaporative cooler : 1 – water tank, 2 – water coil, 3 – water distributor with a catch-drop, 4 – water pump, 5 – air chamber, 6 – drain valve, 7 – control valve with a rotameter

The following tests have been performed with the application of the discussed model:

1. calcium carbonate crystallization on pipes at 40 - 60$^{o}$C,
2. effect of ammonium sulfate on incrustation processes in the model.

Tests have been performed under following conditions: temperature of the pipes 40 and 50-60 $^{0}$C, feeding water parameters (calcium hardness 350 mg $CaCO_3/dm^3$, carbonate hardness 350 mg $CaCO_3/dm^3$, pH 7,2). The deposit has been tested chemically and with the application of a HZGA 2 Carl Zeiss Jena diffractometer.

## EXPERIMENT 1. CRYSTALLIZATION OF CALCIUM CARBONATE

The system has been filled with 10 $dm^3$ of feeding water. A thermostat has been connected to the water circulation system and a pump of circulating water has been switched on. Air stream of $500 dm^3/h$ intensity has been let in. Operation time of the installation has been 5 hours per 24 hours, over the period of 240-hours in total. Makeup water has been supplied as circulating-water losses have been occurring. As the experiment has proceeded a deposit has crystallized and it has been subdued to detailed testing. Photographs of the following crystals: rhombohedral crystals of calcite of the size of a few micrometers, which have crystallized in the temperature of $40^oC$ and sharp-edged rhombic crystals of aragonite, which have crystallized at the temperature of $60^oC$ are presented in Figs 4-5.

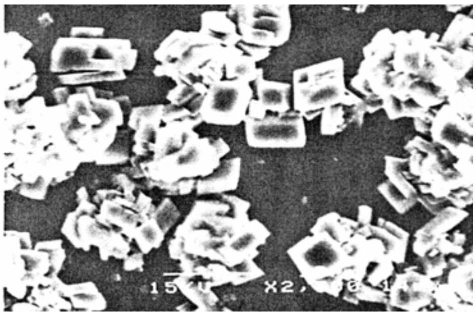

Fig.4. Crystals of calcite

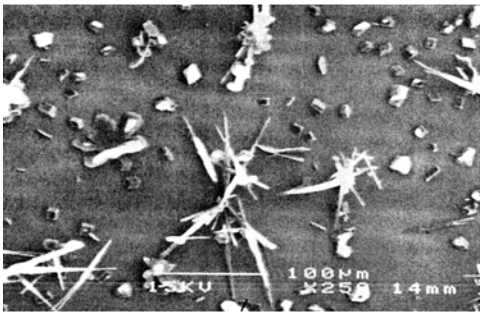

Fig.5. Crystals of aragonite

Figure 6 presents a diffraction pattern of scale that has formed at $40^oC$. A distinct calcite peak can be seen at $26.9^o$ and many other peaks also indicate that the formed deposit is calcite. Other peaks as $20.5^o$, $29.2^o$, $41.5^o$ indicate the presence of monohydrate.

Figure 7 presents a diffraction pattern of scale that has formed at $60^oC$. A distinct calcite peak can be seen at $29.5^o$ as well as numerous aragonite peaks at $26^o$, $27^o$, $32.8^o$ and also monohydrate peaks e.g.. $20.5^oC$.

Recirculating water has been tested once in 24 hours with determining contents of calcium and chlorides in it. Condensation degree $n$ of water has been calculated on the basis of the obtained results:

$$n = \frac{concentration\ of\ chlorides\ in\ circulating\ water}{concentration\ of\ chlorides\ in\ feeding\ water},$$

as well as the calcium hardness ratio *t:*

$$t = \frac{calcium\ hardness\ in\ ciriculating\ water}{calcium\ hardness\ in\ feeding\ water}$$

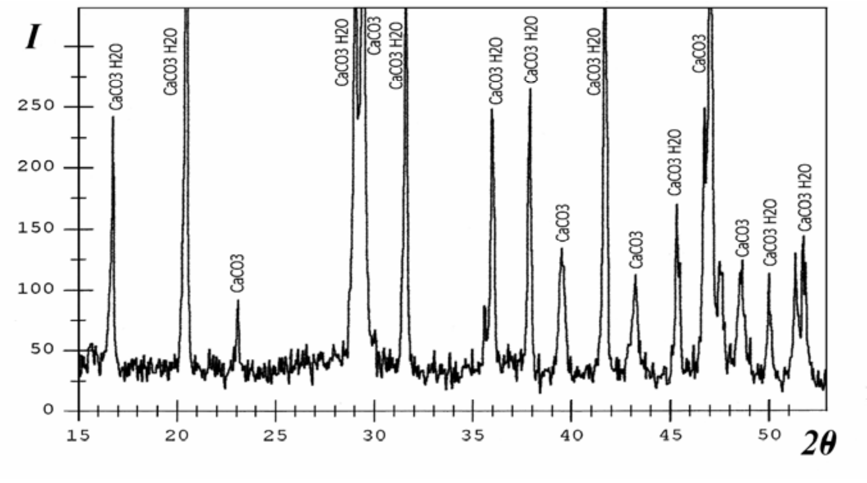

Fig. 6. Diffraction pattern of scale that has crystallized at 40°C

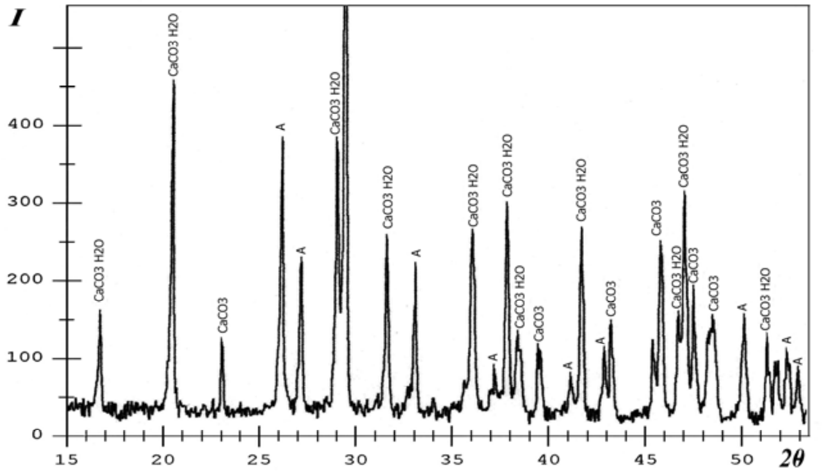

Fig. 7. Diffraction pattern of scale that has formed in the model at 60°C

The $t/n < 1$ ratio shows a loss of $Ca^{2+}$ ions in circulating water as compared to the chloride content and indicates the presence of calcium ions in another form, which means that a solid phase has crystallized (curves 1 in Fig. 8). The pH value of water has increased up to 8.4.

## EXPERIMENT 2. EFFECT OF AMMONIUM SULFATE ON INCRUSTATION PROCESSES

Exactly 4.25 mol/dm$^3$ of $(NH_4)_2SO_4$, has been added to feeding water, which is equivalent to 150% of a stoichiometric dose with respect to the hardness. Pipes of the heat exchanger have been partially covered with scale that formed during the previous experiment performed at 40°C (crystallized calcite).

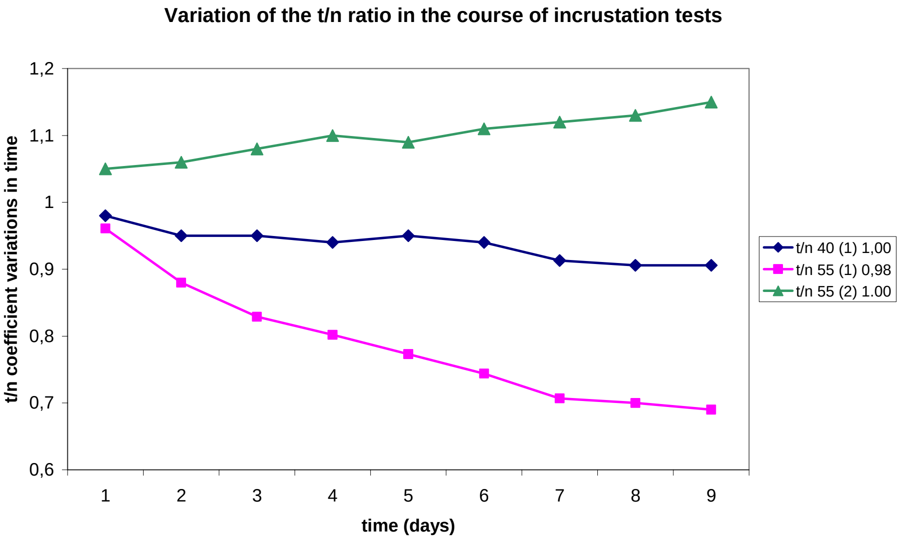

Fig. 8. Variations of the *t/n* ratio in the course of incrustation tests

The testing duration has been 5 hours per 24 hours over the period of 240 hours. Temperature of the pipes has been 60°C. The formed scale has been subdued to diffractometric tests.

Figure 9 shows a diffraction pattern of a scale sample taken when experiment 2 has been completed. The graph shows peaks that are characteristic for calcite, while there are no peaks indicating the presence of aragonite. Calcium sulfate crystals have not been found although the solubility product has been exceeded. When the testing has been completed at the bottom of the circulating water tank tiny chips of scale have been found and they have shown to be calcite.

Recorded values of the condensation coefficients *n* and *t* have shown that the *t/n* ratio has remained contained within the range from 1 to 1.15 (curve 2 in Fig. 8), which means that no further scale buildup has occurred. Calcium ion concentration has been a little higher than it should follow from the condensation level, which indicates that some insignificant chemical dissolution of the scale deposited on the exchanger pipes has occurred. The pH of circulating water has remained at the level of 6.9.

## DISCUSSION

Design of the model makes possible to simulate conditions of an industrial spray-evaporative condenser. An important feature of the model is water recirculation. Temperature of the circulating water differs by ca. 20-25°C from the temperature of the heat exchanger pipes. Air blow cools the water and also makes its evaporation easier by smashing water drops into smaller ones

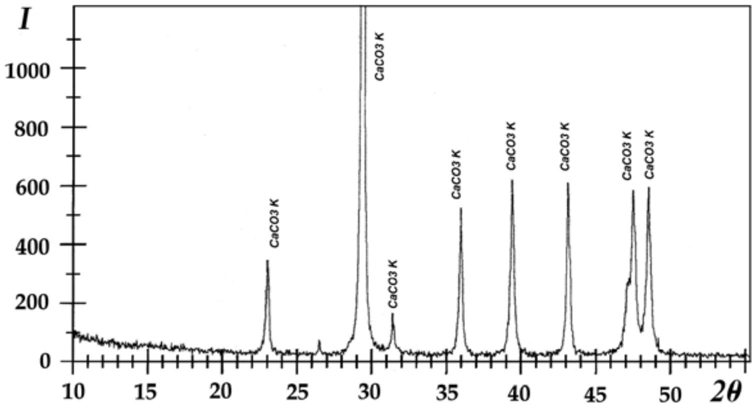

Fig.. 9. Diffraction pattern of scale subdued to the action of $(NH_4)_2SO_4$ at 60°C.

Results of tests performed in the model agree with the literature data (Gomółkowie, 1994; Kowal, 1980; Lipiec and Szmal, 1976). In cooling installations the forming deposit is chiefly calcium carbonate in the form of calcite and monohydrate, while at above $50^0$- $60^0$C a considerable part of the deposit is an unstable aragonite that in some time re-crystallizes into calcite. Crystallization of calcite or aragonite can also be influenced by over-saturation of the solution as well as by the presence of magnesium ions.

The other part of the discussed experiment proves that an addition of ammonium sulfate brings about some insignificant dissolution of the scale (t/n>1), which decisively enhances heat exchange conditions in cooling systems. The selection of an ammonium salt of a strong acid, which hydrolyzes and lightly acidifies the environment, is not accidental, as it eliminates acid, whose overdosage can bring serious corrosive consequences.

An addition of ammonium ions as a biogenic factor is not any shocking in this specific case, as the ammonia presence in a system that includes an ammonia condenser is a obvious because of its leaks to the cooling water resulting from the system leak-tightness faults. The selection of ammonium sulfate to be applied in industrial installations is economically justified, as it is the cheapest of all strong-acid ammonium salts.

In the other experiment calcium sulfate has not crystallized even though the solubility product has been exceeded. According to manuals on chemical analysis calcium sulfate dissolves in the solution of $(NH_4)_2SO_4$, because of the formation of complex compounds according to the following reaction (Lipiec and Szmal, 1976):

$$CaSO_4 + (NH_4)_2SO_4 \rightarrow (NH_4)_2[Ca(SO_4)_2].$$

The reaction runs better under hot conditions and that is why the formation of gypsum on hot walls of a heat exchanger and in the presence of ammonium sulfate is rather unlikely.

## CONCLUSIONS

1. As far as the formation of $CaCO_3$ deposits is concerned, the results of testing performed in the discussed model agree with those given in the pertinent literature. Calcite forms at lower temperatures and aragonite occurs when the temperature exceeds 50°C.
2. The model testing has confirmed what has been observed in other laboratory or industrial installations when ammonium salts have been applied for cooling water treatment purposes (Szymura and Pomianowski, 2005). The dissolution of $CaCO_3$, scale crumbling, and no further formation of new solid phases of calcium sulfate or calcium carbonate is observed, even though the solubility products is exceeded.

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**Szymura T***,* *Badania powstawania kamienia kotłowego w modelowej chłodnicy wodno-powietrznej* Physicochemical Problems of Mineral Processing, 40 (2006), 99-108(w jęz. ang.)

Przedstawiono badania powstawania kamienia kotłowego w laboratoryjnym modelu chłodnicy wodno-powietrznej. Wzorzec takiego wymiennika ciepła jest często spotykany w przemysłowych instalacjach chłodniczych. Wykorzystywana tam nieuzdatniona woda jako nośnik ciepła, pomimo wielu zalet, jest sprawcą wielu problemów, takich jak korozja i inkrustacja. Powstały kamień kotłowy na ściankach wymiennika ciepła powoduje spadek wydajności chłodzenia. Trzymilimetrowa warstwa kamienia obniża wydajność nawet o 60%. Opracowany model pozwala na badania jakościowe i ilościowe powstających na powierzchniach grzejnych krystalicznych osadów. W tym artykule zaprezentowano następujące badania z użyciem modelu chłodnicy; 1. krystalizację fazową węglanu wapnia w temperaturze 30-60$^0$ C. 2. wpływ siarczanu amonu na procesy inkrustacji w modelowym wymienniku ciepła. Badania dyfraktometryczne wykazały różnice w składzie fazowym osadów węglanu wapnia, powstałych w różnych temperaturach i w obecności siarczanu amonu. W temperaturze 30-40$^0$C powstawał węglan wapnia w postaci kalcytu bezwodnego i monohydratu, w temperaturze 55-60$^0$C dodatkowo jako aragonit. Dodany siarczan amonu w dawkach ponad stechiometrycznych powodował , że kamień nie narastał, a nawet nieznacznie się rozpuszczał.