



Article Long-Term Neutralization of Acidic Condensate from Gas Condensing Boilers

Jiří Horák¹, Lenka Kuboňová¹, Milan Dej¹, Jiří Ryšavý¹, Stanislav Bajer¹, Zdeněk Kysučan¹, Pavel Ulrich², Pavel Mareček², Filip Tesař², Martin Garba¹, František Hopan¹ and Petr Praus^{3,*}

- Energy Research Centre, Centre for Energy and Environmental Technologies, VSB-Technical University of Ostrava, 708 00 Ostrava, Czech Republic
- ² Almeva East Europe Ltd., 664 43 Želešice, Czech Republic
- ³ Department of Chemistry and Physico-Chemical Processes, VSB-Technical University of Ostrava, 708 00 Ostrava, Czech Republic
- * Correspondence: petr.praus@vsb.cz

Abstract: The pH of wastewater needs to remain between 6 and 9 to protect water organisms. Condensates from a gas condensing boiler have a pH value of about 3. An optimal way to neutralize the acid condensate is to use cheap material such as dolomite. An old-style neutralization box (NB) was tested with a standard faction of dolomite. However, it did not sufficiently neutralize the condensate. Therefore, several tests were performed involving changes to the construction of the neutralization box, a finer fraction of dolomite and aerating the condensate in the neutralization box. In summary, a new NB technology with partitions, a finer fraction of dolomite and condensate aeration proved sufficient in the neutralization of the pH of the condensate in the short and long terms. It depends on what material the heat exchanger is made of in the condensing boiler. The aluminum content reduces the effectiveness of dolomite in the long run, so aerating the condensate in the NB is recommended, which leads to its more effective neutralization.

Keywords: acidic condensate; neutralization; gas condensing boiler; dolomite; aeration

1. Introduction

Annex No. 15 of the Ministry of Agriculture's Decree No. 428/2001 Coll. [1], which implements Act No. 274/2001 Coll., On Water Supply and Sewerage for Public Use and on Amendments to Certain Acts (Water Supply and Sewerage Act), states the method of determining the permissible degree of pollution in wastewater caused by discharge in the sewerage system. A pH range of 6.0 to 9.0 is permissible in water. According to CSN 756760 [2], condensates generated by combustion with a pH of less than 6.5 should be discharged to domestic wastewater treatment plants, surface water or infiltration plants only after previous neutralization.

Condensates from a gas condensing boiler have a pH value of about 3, which is below the required pH level. At a pH value lower than 4.5, the concentration of bicarbonates and carbonates is negligible. Free carbon dioxide or mineral and organic acids are considered responsible for the acidic character of the water [3].

The first mention of condensate neutralization using limestone was reported by Weast in the *CRC Handbook of Chemistry and Physics* in 1969 [4]. Materials such as soda lime and dolomite were used for condensate neutralization and were mentioned in reports from the Canadian Gas Research Institute GRI 80-0133 by Lahtvee and Shaus [5]. The issue of neutralization was described in detail in 1985 in an article by Harrold [6]. In that research, limestone was used to neutralize the condensate, and neutralizer parameters were processed to calculate the length of the neutralization box/cylinder and a sufficient retention time to effect condensate neutralization.



Citation: Horák, J.; Kuboňová, L.; Dej, M.; Ryšavý, J.; Bajer, S.; Kysučan, Z.; Ulrich, P.; Mareček, P.; Tesař, F.; Garba, M.; et al. Long-Term Neutralization of Acidic Condensate from Gas Condensing Boilers. *Sustainability* 2022, *14*, 15015. https://doi.org/10.3390/ su142215015

Academic Editor: Xinzhe Zhu

Received: 17 October 2022 Accepted: 8 November 2022 Published: 13 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). As described in a previous paper [6], the condensate discharge is 3.8 l/h from a gas furnace with a heat output of about 300 kW. Conversely, the condensate flow rate from a 350 kW gas boiler is about 40 l/h. Therefore, the old neutralization box design is effective for its old parameters; however, it is not suitable for current condensate flow rates. There are two neutralizing unit shape types on the market—box or column. Our study focus has been on finding neutralization units for higher boiler outputs, thus producing higher condensate flow rates. There are several box-shaped neutralization units on the market, especially in the US. Modified neutralization units have also been of interest to us. For example, a neutralization box with baffles was introduced on the Nu-Calgon company website (St. Louis, MO, USA) [7], IBC Technologies, Inc USA website [8] or recently patented [9].

Another parameter influencing the neutralization of condensate may be the type of heat exchanger. In one study, acidic water containing aluminum generated from a condensing thermal power plant was suitably neutralized using a membrane process [10]. Simultaneously, aluminum ions were quantitatively removed, and purified water with an almost neutral pH was obtained. A neutralization unit from the Brilon company (Prague, Czech Republic) uses a column shape, as is apparent online and from their technical documentation [11]. There are differences between the types of neutralization units used, depending on the type of heat exchanger they use (aluminum or stainless-steel). For stainless-steel heat exchangers, the neutralization unit can be used for higher heat outputs in gas condensing boilers; otherwise, aerating the neutralization unit is recommended.

Almeva East Europe Inc. (Zelešice, Czech Republic) has been constantly searching for solutions that are fully functional and practically verified and not only based on theoretical assumptions. There is no technical standard for neutralization boxes in neutralizing acidic condensate flowing out of flue gas paths or condensing boilers. A hypothetical standard would determine how to test these boxes and verify their efficiency. Therefore, we aimed to test the properties and effects of neutralization in the laboratory so that we can market a neutralization box which effect is consistent and functional in practice and, at the same time, meets the pH requirements of sewerage regulations.

The aim of this work was to obtain a neutralization box prototype that would be functional for condensing boilers with an output of up to 500 kW. First, an old-style neutralization box was tested with the standard dolomite fraction. However, it did not sufficiently neutralize the condensate at a higher flow rate. The modified neutralization box technology was based on a new box geometry design, optimizing the condensate flow rate and the particle dimensions of dolomite. Therefore, several tests were performed involving changes to the neutralization box's construction, a finer fraction of dolomite and aerating the NB condensate.

2. Materials and Methods

2.1. Chemical Composition of Natural Gas

Natural gas is a hydrocarbon mixture made mainly of methane and ethane; other hydrocarbons are propane, butane, pentane and hexane. Other gases, together with hydrocarbon gases, are nitrogen, carbon dioxide, hydrogen, noble gases and hydrogen sulfide, as well as other organic sulfur compounds. Sulfur compounds are removed in processing, as they are toxic when inhaled, corrosive to plant and pipeline facilities and become serious pollutants if burned. Mercaptan odorant is always added to commercial natural gas.

In a gas condensing boiler, natural gas is combusted, while water vapor containing CO_2 and as well as other products of combustion is present in a flue gas. The flue gas is cooled down in a heat exchanger, the heating water is warmed up and the waste product is an acidic condensate.

2.2. Analysis of Condensate

Acidic condensates originate from gas condensing boilers using aluminum or stainlesssteel heat exchangers. Aluminum heat exchangers have very high thermal conductivity and a lower price than stainless-steel ones. The drawback of aluminum heat exchangers is fouling deposits, which reduce heat transfer efficiency and cause corrosion.

2.2.1. Complete Analysis of Condensate

A complete analysis of the condensate was performed (Table 1). The condensate was taken from the aluminum and stainless-steel heat exchanger. Inlet means the values of the condensate at the inlet of the NB (before neutralization), and outlet means the values of the condensate at the outlet of the NB (after neutralization).

Parameter	Value	Unit	Measurement Uncertainty	Value	Value	Unit	Measurement Uncertainty	Standard
	Cond 1 Inlet		%	Cond 2 Inlet	Cond 3 Outlet		%	
pН	3.09		± 2.6	3.44	6.33		± 2.6	[12]
inorganic parameters								
ammonia and ammonia salts as NH ₄	3.41	mg/dm^3	± 15.0	1.48	1.39	mg/dm^3	±12	[13,14]
ammoniacal nitrogen	2.65	mg/dm ³	± 15.0	1.151	1.081	mg/dm ³		[13,14]
nitrate nitrogen	62.7	mg/dm ³	± 15.0	19.3	20.4	mg/dm^3		[15]
nitrates	277	mg/dm ³	± 15.0	85.5	90.5	mg/dm^3	± 22	[15]
nitrite nitrogen	0.115	mg/dm ³	± 25.0	0.237	0.234	mg/dm^3		[13,14]
nitrites	0.378	mg/dm ³	± 15.0	0.78	0.77	mg/dm ³	± 13	[13,14]
sulfates as (SO_4^{2-})	37.2	mg/dm ³	± 15.0	14.4	3.29	mg/dm ³	± 18	[15]
chlorides	0.524	mg/dm ³	± 15.0	0.33	0.62	mg/dm^3	± 22	[15]
fluorides	0.267	mg/dm ³	± 15.0	0.2	< 0.05	mg/dm^3		[15]
alkalinity 4.5	< 0.150	mmol/dm ³		0	0.43	mmol/dm ³	± 10	[3,16,17]
alkalinity 8.3	< 0.150	mmol/dm ³		0	0	mmol/dm ³		[3,16,17]
acidity 4.5	2.68	mmol/dm ³	± 15.0	1.82	0	mmol/dm ³	± 10	[18]
acidity 8.3	5.46	mmol/dm ³	± 15.0	2.32	0.25	mmol/dm ³		[18]
organic parameters			± 15.0					
TOC	0.96	mg/dm ³	± 20.0			mg/dm ³		[19]
	3.7			.11 1		1 0 10		

Table 1. Analysis of condensates taken from gas condensing boilers.

Note: Cond 1 = from gas condensing boiler with aluminum heat exchanger. Cond 2, 3 = from gas condensing boiler with stainless-steel exchanger. Inlet—before neutralization; outlet—after neutralization. TIC; carbonates (CO_3^{2-}); bromides; total cyanides, orthophosphates such as P; organic nitrogen; and organic acids (lactic acid, acetic acid, propionic acid, butyric acid @ isobutyric acid, caproic acid, formic acid) were below the measurement limits.

2.2.2. Composition of Dolomite

The composition of the dolomite was provided by the NB producer, which was $SiO_2 = 0.30\%$, $Fe_2O_3 = 0.02\%$, $CaCO_3 = 55.61\%$, $MgCO_3 = 44.20\%$. The tested dolomite comprised irregular-shaped stones of certain fractions. The principle of condensate neutralization by dolomite (Equations (1) and (2)) is as follows:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \tag{1}$$

$$MgCO_3 + 2H^+ \rightarrow Mg^{2+} + H_2O + CO_2$$
 (2)

2.3. Description of Neutralization Box

The old-style version of the NB (Figure 1A) was a plastic box with the external dimensions 276 mm \times 376 mm, using 10 kg of dolomite. The size dimensions of the old-style dolomite fraction were 4–8 mm. A modified version of the NB (Figure 1B) was proposed for the sufficient neutralization of the acidic condensate. To prolong the retention time of the condensate in the NB, the dolomite was crushed and sieved to a 1.8–3.15 mm fraction, for a total weight of 20 kg. Four barriers were added to the old-style NB; the tightness of these barriers was essential for the optimal neutralization of the condensate.



Figure 1. Layout of old-style (A) and modified (B) NB.

2.4. Calculation of Retention Time

To calculate the retention time, it was necessary to know the size of the voids in the dolomite (the grain size of the standard dolomite fraction, 4–8 mm and the modified dolomite grain size of 1.8–3.15 mm). The voids were determined experimentally using distilled water (Table 2) and calculated according to Equation (3).

$$\varepsilon = \frac{m_{water}}{m_{dolomite+water}}$$
(3)

Weight of Crushed Dolomite (g) Weight of Water (g)		Weight of Crushed Dolomite + Water (g)	Voids (%)	
1832	495	2327	21	

Table 2. Experimental determination of voids in modified NB.

Superficial velocity was calculated according to Equation (4):

$$\mathbf{v} = \frac{\mathbf{V}}{\mathbf{S} \cdot \boldsymbol{\varepsilon}} \tag{4}$$

where v is the superficial velocity (m/min), \dot{V} is the inlet flow rate of the condensate (m³/min), S is cross-sectional surface area of the channel in the NB (m²). The channel in the NB is a space separated by a partition; see Figure 1. The retention time is calculated according to Equation (5):

$$=\frac{\mathrm{V}}{\mathrm{S}\cdot\mathrm{v}}\tag{5}$$

where τ is the retention time in the NB (min) and V is the volume of the NB (m³). The mean retention time of the condensate in the modified NB for a condensate flow of 40 dm³/h with voids of 0.21 should theoretically be equal to 3.8 min; see Table 3.

τ

Table 3. Parameters of NB and calculation of superficial velocity and retention time.

Neutralization Box	Standard Dolomite	Standard Dolomite	Modified Dolomite	Modified Dolomite
Weight of dolomite (kg)	10	10	20	20
Particle size of dolomite (mm)	from 4.0 to 8.0	from 4.0 to 8.0	from 1.8 to 3.15	from 1.8 to 3.15
Voids in dolomite (-)	0.31	0.31	0.21	0.21
Width of NB (cm)	26	26	5 ^a	5 ^a
Height of condensate in NB (cm)	15.5	15.5	14	14
Length of NB (cm)	34.5	34.5	172.5 ^b	172.5 ^b
Cross-sectional surface area (m ²)	0.036	0.036	0.007	0.007
Volume of NB (m^3)	0.013	0.013	0.012	0.012
Inlet flow rate of condensate (dm ³ /h)	20	40	20	40
Inlet flow rate of condensate (m ³ /h)	0.02	0.04	0.02	0.04
Superfition velocity (m/min)	0.030	0.060	0.227	0.454
Calculated mean retention time of condensate in NB (min)	11.6	5.8	7.6	3.8

Note: Index "a" means that the width of the NB is the width of one channel in the modified NB, that is, the internal space divided by the barriers. Index "b" means that the length of the NB was multiplied by five because of the five channels in the modified NB.

A more accurate retention time was not determined either theoretically or experimentally. The initial pressure of the condensate, as well as the pressure drop in the NB, was not determined, and neither were the type of flow and the flow rate profile (laminar or turbulent flow according to the Reynolds number).

The retention time for dried dolomite (meaning the voids in the dolomite filled with air) in the modified NB was measured; for a flow rate of $38.4 \text{ dm}^3/\text{h}$, it was equal to 4 min 30 s. The experiment was carried out as follows: (1) The flow rate was set to $320 \text{ cm}^3/0.5 \text{ min at}$ the NB inlet; (2) the NB was connected to a hose with a condensate tank, and the retention time from the beginning of the condensate inlet of the NB and its outlet was measured.

6 of 13

The retention time of the condensate in the hose was negligible compared with the total measured retention time. It was important to know the measured retention time to see if there was any leakage in the NB or within its barriers.

2.5. Methods of Neutralization Tests Measurements

The condensate flow rate through the neutralization box was different during the individual tests and corresponded to the output of the gas condensing boilers for which the neutralization box is intended, in a range of about 70 kW to 500 kW. The condensate flowed from the tank (1 m^3) through the neutralization box filled with 10 kg and 20 kg of dolomite at the selected flow rates (about 20, 40 and 60 dm³/h). At regular intervals, the condensate samples were taken at the inlet of the neutralization box, marked "neutralizer inlet" (at the beginning of each neutralization test), and at the outlet of the neutralization box, marked "neutralizer outlet" (after 15 min of short-term tests and 60 min of long-term tests), and their pH was measured. A pH meter—CyberScan pH 110 (Eutech Instruments)—and a pH probe—CHS PurePro Lab (Chromservis)—were used to measure pH. The pH values were normalized to the same value of the inlet, pH = 3.

3. Results and Discussion

3.1. Principle of Condensate Neutralization by Dolomite

The low pH of the condensate was due to the high concentration of hydrogen ions in the solution. The present anions may correspond to the presence of strong acids in the condensate solution, dissociated to H⁺ and corresponding anions such as SO_4^{2-} , NO_3^{-} , NO_2 and Cl^- (Table 4).

Table 4. Analysis of the anions of strong acids in the inlet and outlet condensates.

Parameter	Unit	Cond 4 (Inlet)	Cond 4 (Outlet, 24 h)	Cond 4 (Outlet, 48 h)	Cond 5 (Inlet)	Cond 5 (Outlet, 24 h)	Cond 5 (Outlet, 48 h)	Standard
pН		2.70	7.11	8.04	2.92	6.87	7.53	[12]
NO_3^-	mg/dm ³	49.891	61.768	61.342	86.144	102.967	99.756	[20]
NO_2^-	mg/dm ³	0.064	< 0.06	< 0.06	1.554	2.130	2.001	[20]
SO_4^{2-}	mg/dm ³	7.812	12.733	11.881	55.397	67.852	63.755	[20]
Cl-	mg/dm ³	0.299	2.304	2.515	0.565	1.793	1.803	[20]

The determination of the pH and anions in the condensate samples after 24 and 48 h of contact with dolomite in a ratio of 4 g per 100 mL condensate (1:25) was performed to influence changes in the original values after the condensate interacted with the dolomite. An increase in pH to almost neutral values after 24 h was recorded; after 48 h, the condensate was weakly basic. The concentration of nitrate, nitrite, chloride and sulfate anions increased visibly after 24 and 48 h. This could be due to the release of impurities from the dolomite. The analysis clearly showed that dolomite only served to adjust the pH and the investigated anions that were released from it.

3.2. Neutralization of Condensate from Aluminum Heat Exchanger

In the case of the condensate flowing through the bed, achieving neutralization can be influenced by: (1) the height of the bed (amount of dolomite) through which the condensate flows; (2) the flow rate of the condensate through the dolomite bed; and (3) the contact time of the condensate with dolomite.

3.2.1. Dynamic Short-Term Test of pH Changes in the Condensate Caused by the Standard Dolomite

The change in the pH of the condensate as a function of its flow rate through the neutralization box is shown in Figure 2.



Figure 2. Change in the condensate's pH dependent on the condensate flow through (i) the old-style NB with the standard dolomite fraction size (4.0–8.0 mm) (black) and (ii) the modified NB with barriers and dolomite fraction size (1.8–3.15 mm). Note: The retention time of the condensate in the modified NB filled with dry dolomite was 4 min 10 s with a flow rate of 38 dm³/h. Note: Black and grey lines are measured values, red lines are standard deviations.

From the test results, it is evident that the condensate neutralization was satisfactory, occurring at a flow rate of $6.0 \text{ dm}^3/\text{h}$ and $6.5 \text{ dm}^3/\text{h}$ when the average pH value of the condensate at the outlet of the neutralization box was 6.2. In other cases, the pH was less than 6. The flow rates of $6.0 \text{ dm}^3/\text{h}$ and $6.5 \text{ dm}^3/\text{h}$ correspond to the heat output of 53 kW and 57 kW gas condensing boilers, respectively, which are below the required lower limit (70 kW).

3.2.2. Dynamic Short-Term Test of pH Change in the Condensate Caused by the Modified Dolomite

There was a neutralizing mixture in the NB (dolomite crushed to a grain size of 1.8–3.15 mm) weighing 20 kg. The change in the pH of the condensate depended on the NB flow, as shown in Figure 2.

The average pH of the condensate at the inlet of the NB ranged between 2.9 and 3.0, which is within the measurement uncertainty. This NB arrangement and connection variant was tested only for a maximum flow rate, and the test results of this connection show that the condensate was satisfactorily neutralized. The average pH of the condensate at the highest flow rate of 40 dm³/h was 6.40. A flow rate of 45 dm³/h was experimentally chosen with an average pH of 6.43, and an average pH of 6.39 was chosen for a flow rate of 58 dm³/h.

A 12 h test was also performed for a flow rate of 40 dm³/h and 20 kg of crushed dolomite, which resulted in the sufficient neutralization of the condensate (pH > 6). According to the manufacturer's requirements, a long-term condensate neutralization test (15 h) was also performed, with the pH decreasing over time. The dolomite was, therefore, washed and dried in an oven at 80 °C. The short-term test was repeated, and we confirmed that this step was beneficial for the activation of dolomite; again, there was sufficient neutralization of the condensate (pH > 6 at a flow rate of about 40 dm³/h). The retention time of the condensate in the NB with dried dolomite was effective. A condensate neutralization test was performed for a flow rate of 59 dm³/h, and the neutralization was sufficient (pH > 6).

3.2.3. Dynamic Long-Term Test of pH Change in Condensate in NB

A long-term condensate neutralization test in the NB was performed within four working days. As can be seen from Figure 3, the steady-state pH (pH of the condensate that flowed out of the NB after the night shutdown) and the pH in the dynamic state (pH of the condensate that flowed out of the NB continuously after the inlet and outlet flow stabilized) decreased over time, so the dolomite was deactivated by covering the dolomite particles with aluminum ions (as described below).



modified NB_Al heat exchanger_long term test

Figure 3. Long-term neutralization test on condensate from the aluminum heat exchanger in the modified NB (the condensate flow rate was 38 dm³/h). Note: The dashed lines represent the division between the previous day and the following day of measurement.

After this long-term test, the dolomite was dried again (80 °C), and from the beginning of the test there was a decrease of approx. 2.5% in the total dolomite weight before the neutralization test. The dissolution of the dolomite was not visually apparent. Then, a short-term neutralization test was performed, and we found that the dolomite was again active after drying (pH = 6.6 after stabilization with an outlet flow rate of 38 dm³/h).

3.3. Improvements in Condensate Neutralization

3.3.1. Aeration of Condensate in NB

Dissolved salts and gases in the condensate can be removed by aeration. Mixing water and air oxidizes these salts and makes them filterable. Carbon dioxide is also removed during aeration by establishing equilibrium between water and air by aeration. Increasing the temperature would lead to a higher removal of gases by aeration [21].

A long-term, one-day test was performed in the NB with aeration via aquarium stones (TetraTec AS) (Figure 4). Ten 15×25 mm aquarium stones and 4 and 5 mm diameter connecting silicone tubes were added to the compressor (the air flow rate was about $185 \text{ dm}^3/\text{h}$). The retention time for the dried dolomite was over 4 min, which confirmed the experimental results from the previous test. As can be seen from Figure 4, the pH decreased slightly during the one-day test, but the pH was still above the desired limit (pH > 6).



Figure 4. Changes in condensate pH and concentration of TOC and Al (mg/dm^3) over time during flow through the NB (modified NB; aeration; flow rate of condensate, 38 dm³/h).

One of the reasons why the pH gradually decreased in the previous long-term tests was the presence of Al in the acidic condensate. Figure 4 shows that during the neutralization there was a decrease in the initial concentration of Al from 16 mg/dm³ to 0.79 mg/dm³ approx. 30 min after the start of neutralization. Within the measurement deviation, this value was maintained throughout the one-day bubble neutralization test.

The presence of organic compounds was verified by analyzing the total organic carbon (TOC), which decreased from the input value of 6.1 mg/dm^3 to 4.3 mg/dm^3 after more than 6 h of neutralization. The higher TOC concentration value of 12.7 mg/dm^3 was probably due to the leaching of trapped TOC from previous tests that did not evaporate when the dolomite was dried to 80 °C.

3.3.2. Analysis of Total Organic Carbon

According to the Czech government decree No. 401/2015 Coll. [22], the acceptable limit for TOC in surface water is 10 mg/dm³ as an annual average based on permissible surface water and wastewater pollution indicators and values, requirements which are relevant to permits regarding discharged wastewater in surface waters, sewers and other sensitive areas. Therefore, the condensate samples were measured at the inlet as well as at the outlet after neutralizing them in the NB. The concentration of TOC in the condensate at the inlet was below the annual average limit concentration; see Table 5.

		Condensate at Inlet of NB	Condensate at Outlet of NB (K0)	Condensate at Outlet of NB (K1)	Uncertainty
Parameter	Unit				
pH (not normalized)	-	3.7	7.08	7.22	$\pm 4\%$
TOC	mg/dm ³	6.1	12.7	5	$\pm 20\%$
Al	mg/dm ³	16	2.92	0.79	$\pm 8\%$

Table 5. Analysis of Al concentration (mg/dm³) for inlet and outlet condensate samples.

Note: Condensate K0 is measured at the outlet of the NB right after measuring the retention time; condensate K1 is measured at the outlet of the NB after stabilizing the flow (inlet = outlet).

3.3.3. Analysis of Aluminum

The aluminum concentrations in natural waters ranged from 0.001 to 0.05 mg/dm³ at a pH approaching neutral and up to 0.5-1 mg/dm³ in acidic condensates and water

rich in organic substances. In extremely acidic waters, such as mining water, aluminum content can reach values of up to 90 mg/dm³ [23]. The acceptable limit for aluminum from various sources, such as the production and processing of precious and non-ferrous metals, is 3 mg/dm³ according to Czech government decree No. 401/2015 Coll. [22].

Three condensate samples were analyzed at the inlet of the NB, at the outlet after measuring the retention time (-K0) and at the outlet after stabilizing the flow (inlet = outlet - K1); see Table 5. It is evident from the results that the concentration of Al in the inlet condensate was high and above the Czech legislative limit. However, during the gradual flow of the condensate, the sorption of Al on the surface of the dolomite likely takes place, and thus, the Al ions are removed.

3.3.4. Use of Siphon and the Aeration of the Condensate

The NB was filled with condensate overnight (siphon principle) and aerated (Figure 5). The aeration, together with the siphon, had a supportive character in neutralizing the condensate in the NB due to the removal of carbon dioxide according to Equations (1) and (2).



---modified NB_Al heat exchanger_no aeration ---modified NB_Al heat exchanger_aeration

Figure 5. Effect of aeration on neutralization of condensate from the aluminum heat exchanger (flow rate of condensate $38 \text{ dm}^3/\text{h}$).

3.4. Neutralization of the Condensate from Stainless-Steel Heat Exchanger

Dynamic Long-Term Test (3 Days) of pH Changes in the Condensate in the NB

To verify our assumptions about the problematic neutralization of the condensate with higher Al content, the condensate was collected from the stainless-steel exchanger. The amount of Al from this condensing boiler was 2.3 mg/dm³, taken directly in the boiler room. Long-term tests were then performed (Figure 6).



modified NB_steel heat exchanger_long term test

Figure 6. Long-term test on condensate neutralization in a stainless-steel heat exchanger using the modified NB (flow rate was 59 dm³/h through the NB). Note: The retention time was 3 min 14 s. In total, approx. 0.6% of the dolomite dissolved, and below the crushed fraction the dolomite amounted to 4.6% before the neutralization test. The dashed lines represent the division between the previous day and the following day of measurement.

When neutralizing the condensate from the stainless-steel exchanger, the dolomite also neutralized higher condensate flows, but over time, the pH decreased again, with a difference of approx. 0.2 after stabilization the next day.

The same NB aeration connection was also used for the $59 \text{ dm}^3/\text{h}$ condensate flow from the stainless-steel exchanger (Figure 7).



--- modified NB_steel heat exchanger_no aeration --- modified NB_steel heat exchanger_aeration

Figure 7. Effect of aeration on condensate neutralization from stainless-steel heat exchanger (the flow rate was 59 dm³/h through the NB).

From Figures 5 and 7, it can be seen that aeration had a positive effect on condensate neutralization. However, the pH should be controlled regularly, and in cases of a decreased pH value, reactivating dolomite by washing and drying it at a minimum temperature of 80 °C is required.

4. Conclusions

A detailed research study was conducted to modify neutralization box (NB), neutralizing agent (dolomite) and process of neutralization to fulfill the requirements for a new neutralization unit. The modified neutralization box improved the neutralization of the acidic condensate from the gas condensing boilers in comparison with the old-style NB design. The modified technology is suitable for higher condensate flow (higher heat output of gas condensing boilers) and long-term neutralization.

The modifications were based on prolongation of retention time of the condensate by addition of partitions in the NB and obtaining a finer fraction of dolomite (1.8–3.15 mm). The retention time of the condensate in the NB is an important parameter for long-term neutralization.

The different composition of condensate influenced the effectiveness of neutralization. In particular, the content of aluminum was studied. Condensates with lower Al content (from stainless-steel exchangers) can be neutralized at higher flows. In the long-term run, the aeration of the condensate either from aluminum or stainless-steel heat exchangers had a positive effect on the process of neutralization.

The efficiency of dolomite in the NB decreased in the long-term run, which was due to the deactivation of dolomite. There was also a gradual dissolution of dolomite (this was not visually apparent). The dolomite was reactivated at a minimum of 80 °C. Before drying, it is possible to wash the used dolomite with distilled or clean water.

Author Contributions: Conceptualization, J.H., P.U., P.M. and F.T.; methodology, J.H. and M.D.; software, M.G.; validation, L.K. and S.B.; formal analysis, M.D. and Z.K.; investigation, L.K., S.B. and Z.K.; resources, J.H., P.U., P.M. and F.T.; data curation, L.K. and S.B.; writing—original draft preparation, L.K. and P.P.; writing—review and editing, P.P., J.R. and F.H.; visualization, L.K.; supervision, J.H. and M.D.; project administration, P.U., P.M. and F.T.; funding acquisition, P.U., P.M. and F.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The problem of the neutralizing condensates formed by condensation from flue gases due to natural gas combustion was instigated by Almeva East Europe Inc., which was also the initiator of this research.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Ministry of Agriculture of the Czech Republic. Annex No. 15 to Decree of the Ministry of Agriculture No. 428/2001 Coll., which Implements Act No. 274/2001 Coll., On Water Supply and Sewerage for Public Use and on Amendments to Certain Acts (Water Supply and Sewerage Act). Available online: https://www.zakonyprolidi.cz/cs/2001-428 (accessed on 3 November 2022).
- 2. CSN 756760; Drainage Systems Inside Buildings and on Private Ground. Czech Standardization Agency: Prague, Czech Republic, 2014.
- 3. CSN 757373; Water Quality—Calculation of Carbon Dioxide Forms (Species). Czech Standardization Agency: Prague, Czech Republic, 2001.
- 4. Weast, R.C. CRC Handbook of chemistry & Physics, 50th ed.; The Chemical Rubber Co.: Cleveland, OH, USA, 1969.
- 5. Lahtvee, T.; Schaus, O.O. *Study of Materials to Resist Corrosion in Condensing Gas Furnaces*; Canadian Gas Research Institute Report GRI 80-0133; Gas Research Institute: Chicago, IL, USA, 1982.
- Harrold, D.E.; Baumann, E.R. Characterization and treatment of condensates from high efficiency appliances. *Water Res.* 1985, 19, 627–638. [CrossRef]
- pH Treat of Nu-Calgon. Available online: https://www.nucalgon.com/products/water-treatment/other-water-treatment/phtreat/ (accessed on 1 October 2022).
- Condensate Neutralization Kit—IBC Technologies Inc. USA. Available online: www.ibcboiler.com/consumer/products/ accessories/condensate-neutralization-kit/ (accessed on 3 November 2022).
- 9. Bernasconi, M.C. Condensate Neutralizer: United States Patent Application Publication. U.S. Patent 2020/0103141 A1, 2 April 2020.

- Nafliu, I.M.; Grosu, A.R.; Al-Ani, H.N.; Albu, P.C.; Gheorghievici, G.; Craciun, M.E. Neutralization with simultaneously separation of aluminum ions from condensate water through cellulose derivatives-capillary polypropylene composite membranes. *Mater. Plast.* 2019, 56, 301–305. [CrossRef]
- 11. Neutralization Box Neutrakon. Available online: https://www.neutrakon.cz/ (accessed on 1 October 2022).
- 12. ISO 10523:2008; Water Quality—Determination of pH. International Organization for Standardization: Geneva, Switzerland, 2008.
- 13. EN ISO 11732:2005; Water Quality—Determination of Ammonium Nitrogen—Method by Flow Analysis (CFA and FIA) and Spectrometric Detection. International Organization for Standardization: Geneva, Switzerland, 2005.
- 14. EN ISO 13395:1996; Water Quality—Determination of Nitrite Nitrogen and Nitrate Nitrogen and The sum of Both by Flow Analysis (CFA and FIA) and Spectrometric Detection. International Organization for Standardization: Geneva, Switzerland, 1996.
- 15. *ISO 10304-1:2007;* Water Quality—Determination of Dissolved Anions by Liquid Chromatography of Ions—Part 1: Determination of Bromide, Chloride, Fluoride, Nitrate, Nitrite, Phosphate and Sulfate. International Organization for Standardization: Geneva, Switzerland, 2007.
- 16. ISO 9963-1:1994; Water Quality—Determination of alkalinity—Part 1: Determination of Total and Composite Alkalinity. International Organization for Standardization: Geneva, Switzerland, 1994.
- 17. ISO 9963-2; Water Quality—Determination of Alkalinity—Part 2: Determination of Carbonate Alkalinity. International Organization for Standardization: Geneva, Switzerland, 1994.
- ČSN 75 7372; Water Quality—Determination of Base Neutralizing Capacity (Acidity). Czech Standardization Agency: Prague, Czech Republic, 2001.
- 19. *EN 1484:1997;* Water Analysis—Guidelines for the Determination of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DIC). European Committee for Standardization: Brussels, Belgium, 1997.
- US EPA Method 1011B; Determination of Ion Chromatography Anions with Conductivity Detection. United States Environmental Protection Agency: Washington, DC, USA, 1989.
- 21. Vakkilainen, E.K. Steam Generation from Biomass. Construction and Design of Large Boilers; Elsevier Inc.: Oxford, UK, 2017; pp. 180–202.
- Decree of the Czech Government No. 401/2015 Coll. on Indicators and Values of Permissible Surface Water and Wastewater Pollution, Requirements for Permits for Discharge of Wastewater into Surface Waters and Sewers and on Sensitives Areas. Available online: https://www.zakonyprolidi.cz/cs/2015-401 (accessed on 3 November 2022).
- Houšková, L. Frakcionace Hliníku při Vodárenské Úpravě (Translation to English: Fractionation of Aluminum in Water Treatment). Bachelor's Thesis, Charles University, Prague, Czech Republic, 2010.