

Article

Waste Incineration and Heavy Metal Emission—Laboratory Tests

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Abstract: The main sources of environmental pollution with heavy (ecotoxic) metals include industry, including utility and municipal power engineering, but also waste incineration plants. Fuel shortages and their constantly growing prices raise concerns that energy will be commonly obtained from waste outside of installations intended for this purpose (i.e., outside waste incineration plants). The greatest concern stems from the risk of burning waste in low-power boilers—domestic boilers. Waste incineration plants and utility power plants are equipped with flue gas cleaning installations (FGD), but low-power boilers are not. The exhaust gases are directly introduced into the atmosphere, which results in the introduction into the air of, inter alia, toxic heavy metals. Therefore, it is necessary to conduct activities aimed at retaining ecotoxic metals in the solid-slag residue. The paper presents the results of laboratory tests of the emission capacity of Cd, Cu, Zn bound in various chemical forms—nitrates (V), chlorides and sulphates (VI). The tests were carried out at 1073 K, 1173 K and 1273 K. It was found that the emissivity of metals increased with increasing temperature. This is innovative as there are no reports of experiments with pure forms of metal salts. The advantage of this type of research is the lack of influence from other factors, apart from temperature, on metal emissions. To check the possibility of reducing metal emissions, additives (bauxite, dolomite, V₂O₅) immobilized in a solid residue were tested. The mechanism of action of each of the additives to limit the mobility of metals was different. The use of V₂O₅ for this purpose is new. The additives kept the metals solid in the residue, but their effect was different for each of the metals. The effectiveness of the tested additives was checked in the same temperature conditions, burning waste such as: rubber, sewage sludge and SRF fuel from waste. The effect of the additives depended on the type of waste, type of metal and the furnace temperature. If the additive effectively retained metals, then their amounts in the ashes were higher by several to several dozen percent in relation to the amount in the ashes remaining after waste incineration without additives. The results of the experiment with waste are open to research on the influence of other factors (except temperature) on the emissivity of Cd, Cu, Zn and the possibility of its reduction. The next step will be to verify the effects of laboratory tests in real conditions.

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1. Introduction

Heavy metals (term not accepted by the International Union of Pure and Applied Chemistry IUPAC; according to the current nomenclature, they should be called ecotoxic metals) in various forms are naturally dispersed in the environment. Their concentration is the background. Concentration values depend on the continent and country, region and zone. Concentrations higher than background in a given area indicate environmental pollution. The natural cycle of elements in nature maintains a state of equilibrium between the amount released and introduced into the biological environment and the amount

bound and deposited in geological formations. Various human activities disturb the natural geochemical cycle. The main source of pollution with ecotoxic metals is industry, including utility and municipal power engineering—fuel combustion processes, but also waste incineration plants. The generation of energy in combustion technologies, especially solid fuels and waste, causes the emission to the environment of many harmful and toxic substances, such as HCl, SO₂, PAH, PCDD and ecotoxic (heavy) metals. The emission of metals that exhibit different activity in the furnace during combustion is of great importance. This necessitates the constant control of the emissions of ecotoxic metals introduced into the environment and the construction of installations ensuring combustion processes with minimal emission to the atmosphere.

The current difficult situation on the fuel market in Europe (and, therefore, in Poland)—shortages of coal, biomass and their constantly growing prices—raises concerns that energy will be obtained from waste outside of installations intended for this purpose (i.e., in units other than waste incineration plants). The greatest concern stems from the risk of burning waste in low-power boilers—domestic boilers. While waste incineration plants and utility power plants are equipped with flue gas treatment (FGD) installations, low-power boilers are not. The exhaust gases are directly introduced into the atmosphere.

Ecotoxic metals are present in all types of waste in various concentrations and forms. In the combustion chamber, the intensity of the evaporation of metals and their compounds, apart from their vapor pressure, depends on many complex and interrelated factors such as temperature, oxidizing or reducing conditions and the presence of halides. Metals emitted to the atmosphere from waste incineration systems may adsorb on the surface of dusts, fly ash or exist as individual particles, posing a potential threat to human health. It is well known [1–5] that heavy metals pose a serious toxic threat and burden to the natural environment, which exposes people to disease processes that are dangerous to life. Metals are very often emitted as particles smaller than 1 µm. Gas stream cleaning devices are less effective at capturing such small particle sizes than larger particles. These tiny particles can travel to the lungs where poisonous metals come into contact with the blood. Therefore, an important role is played by the possibility of retaining ecotoxic metals in the solid-slag residue.

Ref. [6] describes the research carried out in an installation designed to incinerate municipal waste from the MSW. The focus was on the influence of the diverse composition of the MSW, and heavy metal emissions were investigated for various operational parameters such as: air-fuel ratio and process temperature. The influence of the presence of sulfur and chlorine during the combustion of MSW was also investigated. During the thermal utilization of troublesome sewage sludge, metals such as As, Cr, Zn and Cu are emitted into the atmosphere [7]. Studies on limiting volatilization of these metals (except As) to the atmosphere by sorption are presented in [7,8]. Calcium sorbents CaO and CaCO₃ were used. The process of capturing Cr, Zn and Cu was tested in the conditions of a boiler furnace at temperatures of 700–1150 °C. A wider scope of research with the use of calcium sorbents is presented in [9]. The authors burned food waste in the oxy-fuel technology, where Zn and Cr were effectively retained by adding sorbents to the furnace. Laboratory tests in a tube furnace [10] showed that by using CaO, the emission of Cu, Ni, Zn was effectively reduced during the combustion of rubber and polyethylene waste. The authors indicated different efficiencies for capturing these metals in the furnace chamber, at different combustion temperatures. The innovative technology of biomass and municipal waste combustion is presented in [11]. Using the technology of oxygen carrier aided combustion (OCAC), which uses ilmenite as bed material, the behavior of zinc, copper and lead was investigated. Iron contained in ilmenite actively participated in the process of binding Cu and Zn. It was found that Pb interacts with the titanium in ilmenite to form PbTiO₃, while Cu and Zn interact with ferrites to form CuFe₂O₄ and ZnFe₂O₄. In [12], during the combustion of solid fuels, the behavior of Si- and Ca-based sorbents in the process of heavy metals (Pb, Cd and Cr) capture, in the presence of HCl and SO₂ in flue gases, was investigated. It was found that among tested sorbents, kaolin turned out to be the most

effective in capturing Pb and Cd. When they incinerated dried sewage sludge with kaolin addition, Pb and Cd were shifted from sub-micron to macro-sized particles, accompanied by a considerable decrease in 0.1 μm particles. Furthermore, [13] presents a parametric study that shows the effect of temperature on the global process of heavy metal vaporization (evaporation) during municipal waste incineration. The process was described by a numerical model. Then the model was verified on a test stand. Heavy metal emission tests: Sb, As, Cd, Co, Cr, Cu, Pb, Mn, Ni, Tl, V, Hg and Zn during combustion of birch and pine/spruce, birch and pine bark, oat grains, peat and coal stone are presented in [14]. Compared to coal and peat, biomass fuels generated higher Zn emissions but lower or close to the sum of other metals.

The aim of the study was to check the mobility and to determine the conditions and dependencies determining the transition of selected ecotoxic metals to the gas phase. The study of behavior at various temperatures and media, as well as forms, was assumed to be carried out for metals Cd, Cu, Zn in the form of salts: chlorides, nitrates (V) and sulphates (VI). Based on the results of these studies, additives were selected (with different mechanisms of action), which, at high temperatures, may cause greater immobilization of metals in the slag.

The literature presents research works related to emissivity in the combustion processes of ecotoxic metals present in fuels or waste. There are no studies conducted with pure metal salts exposed to high temperatures as research material. The authors of this work took up such a challenge. This type of research is innovative in this context. They related knowledge concerning the behavior of bound metals in the form of their salts without the influence of other factors (elements) that are present in combustible materials. It should be clearly noted that in the case of combustion of specific materials—fuels or waste, in which heavy metals are present, speciation analyses are not performed for these materials to determine the chemical forms of the metals in which they are bound. In addition, testing of metal immobilizing additives in the ash residue has enriched the knowledge about the possibility of reducing heavy metal emissions from combustion processes.

The research on the behavior of these metals, as well as the influence of immobilizing additives, was checked in laboratory conditions by determining the metal emissions in the waste incineration process. Such studies show that the emission of metals is influenced, apart from temperature, by other factors related to the nature of the combustible material. Research on the impact of individual factors on the emission of heavy metals may be the subject of further studies and analysis of the results. Metal emission tests during waste incineration and metal immobilization can be further verified at semi-technical and then technical scale facilities.

2. Materials and Methods

The research covered the following ecotoxic metals: cadmium (Cd), copper (Cu), zinc (Zn). The conducted experiment consisted of two parts. First, the emission abilities of bound metals in the form of chlorides, nitrates (V) and sulphates (VI) and a mixture of chlorides, which were individually applied to the refractory inert matrix—zircon (IV) oxide, were investigated. In this case, the idea was to eliminate the influence of other elements that are present in macro amounts in fuels or waste. The investigated metals may change into more volatile forms during combustion in transformation processes. Samples of metal compounds were exposed to temperatures of 1073, 1173, 1273 K. The tests were carried out for each metal and for each form separately and for a mixture of chlorides of all three metals. Mutual interactions were checked with a sample of the chloride mixture of all metals. In order to limit the gaseous emission of metals, immobilizing additives were used: divanad pentoxide, bauxite, dolomite.

The second stage consisted of examining the behavior of metals present in waste (during waste incineration)—municipal sewage sludge, fuel from waste type SRF [15], rubber from waste car tires. In this cycle, the same additives immobilizing heavy metals

in the solid residue were also used. The action of the additives at high temperatures was to reduce the transfer of metals to the gas phase. The choice of additives was dictated by a different mechanism of action. Divanad pentoxide forms thermally stable vanadates at high temperatures. Bauxite is a flux that allows heavy metals to be retained (sinking) at high temperatures. Dolomite has a sorption effect and also binds chlorine (chlorine transformation can form volatile chlorides with metals).

All experimental trials were repeated three times to eliminate big errors. The given results are the arithmetic mean.

2.1. Materials

CdCl₂ anhydrous p.a., CdSO₄ anhydrous p.a., CuCl₂ anhydrous p.a., CuSO₄ anhydrous p.a., ZnCl₂ anhydrous p.a. and ZnSO₄ • 7H₂O p.a. were supplied by Sigma Aldrich. CdNO₃ anhydrous p.a., CuNO₃ anhydrous p.a., ZnNO₃ • 6H₂O p.a., boxite and dolomite were supplied by POCH Poland. Matrix: zircon (IV) oxide, grain size < 40 µm, manufactured by the Institute of Ceramics and Building Materials, Division of Fireproof Materials in Poland. Divanadu pentoxide V₂O₅ p.a. was produced by LOBA Feinchemie Austria. Sewage sludge—from municipal sewage treatment plants in Poland, grain size up to 5 mm. SRF fuel—from a plant producing fuels from the combustible fraction of municipal and industrial waste, grain size less than 35 mm. Rubber from waste car tires—used car tires were stripped of textile cord and reinforcement, and the rubber was crushed to a grain size of up to 5 mm.

2.2. Preparation of Samples of Cd, Cu, Zn Metal Salts and Measurement of the Concentrations of These Metals in the Samples

Each type of salt (chloride, nitrate, sulphate) of each of the tested metals (Cd, Cu, Zn) was individually introduced into the inert matrix—zircon (IV) oxide, in amounts of approximately 500 ppm of metal, thoroughly homogenized in an agate mortar. The sample in which the matrix contained a mixture of chlorides of all metals was also prepared in an identical manner. A series of tests as above was also prepared in which, apart from metal salts, immobilizing additives were introduced individually: divanad pentoxide, bauxite, dolomite in the amount of 1% by weight.

Next, the metal content in each sample (Table 1) was determined using the flame atomic absorption spectrometry (FAAS) method (AAS by Perkin Elmer), previously wet mineralizing the samples according to generally accepted procedures. An acetylene–air flame (oxidizing) was used for all elements, nebulization efficiency 5.5 cm³/min. The samples for determination were weighed on an analytical balance with an accuracy of 0.0001 g. A blank test was performed for each series of tests.

Table 1. Initial concentrations of metals in samples of nitrates (V), chlorides, sulphates (VI) and in a mixture of chlorides.

A Type of Metal Salt	Metal [ppm _m]		
	Cd	Cu	Zn
nitrate (V)	366	428	499
chloride	570	394	419
sulphate (VI)	553	403	535
mixture of chlorides	546	467	496

2.3. Determination of Physicochemical Properties and Cd, Cu, Zn Concentrations in Tested Waste

Wastes, as in point 2.1., were ground in an IKA WERKE electric mill. They were dried to a constant weight at 378 K. The ash content was determined in accordance with PN-EN 15403: 2011, CHNS elemental analysis was performed with the Perkin Elmer elemental analyzer, chlorine was determined according to PN-ISO 587/2000 (Table 2).

Table 2. Physicochemical properties of waste.

Type of Waste	Ash [%]	Carbon c^{daf}	Hydrogen h^{daf}	Nitrogen n^{daf}	Sulfur s^{daf}	Chlorine cl^{daf}	Oxygen o^{daf}
sludge	39.9	33.0	4.4	4.9	1.7	0.1	55.9
rubber scrap	10.2	85.0	7.5	3.9	1.6	0.0	2.0
fuel from waste type SRF	11.3	49.0	1.9	0.6	0.4	0.4	47.7

The content of Cd, Cu, Zn metals in all three types of tested waste (Table 3) was determined with the Perkin Elmer AAS atomic absorption spectrometer as in point 2.2.

Table 3. Concentrations of metals in waste.

Type of Waste	Cd [ppm _m]	Cu [ppm _m]	Zn [ppm _m]
sludge	21	161	2791
rubber scrap	2.5	48	17,095
fuel from waste type SRF	1.4	433	566

2.4. Furnace

The muffle furnace, in which the metal emission tests were carried out, has a drawer in which the samples are placed. The furnace has a temperature setting of max. to 1373 K. Air is supplied to the combustion chamber. After the combustion chamber is heated to the desired temperature, the drawer with the sample is inserted.

The tests were carried out successively at the temperatures of 1073 K, 1173 K and 1273 K. The air flow rate was 10 dm³/min. The view of the furnace is shown in Figure 1.

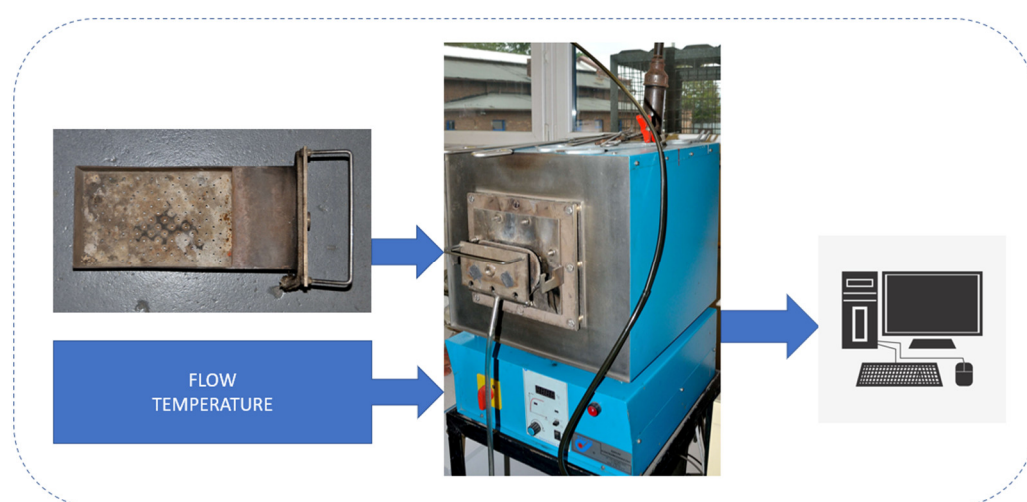


Figure 1. Test muffle furnace.

2.5. Research on the Behavior of Cd, Cu, Zn Metal Salts at High Temperatures

From samples prepared as in point 2.2., weights were prepared on an analytical balance (50 g each) with an accuracy of 0.0001 g. Weighed samples in the muffle furnace (point 2.4) were subjected to high temperatures, successively, 1073, 1173, 1273 K.

After the end of the ignition, the metal concentrations in the samples were determined as in point 2.2.

2.6. Research on the Behavior of Cd, Cu, Zn Metals that Constitute Waste Contamination in Waste Incineration Processes

Wastes, as in point 2.1. were dried to a constant weight at 378 K. Then, 50 g of samples were weighed (with an accuracy of 0.0001 g), and then they were burnt in a muffle furnace at the following temperatures: 1073, 1173, 1273 K. The residence time of the sample in the high-temperature zone was defined as the limit of measurable, minimal weight loss. The amount of metals, which were not removed from the furnace in the gaseous emission in the non-flammable residue, was determined.

Then, the additives of divanad pentoxide, bauxite and dolomite (point 2.1) were added individually in the amounts of 1 and 2% to the waste samples. The samples were burned in a muffle furnace at the same temperatures, successively, 1073, 1173, 1273 K. The amount of metals remaining in the ash, which was not removed from the furnace in the gaseous emission, was determined.

3. Results and Discussion

In order to present graphically the dependence of the gaseous emissions of individual metals (in the series where the metals Cd, Cu, Zn are in the form of their salts and in the series where the metals are contaminated in the waste) on the temperature of thermal transformation of the samples, Figures 2–8 were prepared. The graphs show the effect of additives on the binding and immobilization of metals in the ash. On the ordinate axis, there are the test roasting temperatures [K], and on the abscissa axis, the values of the C_i/C_0 ratio, where:

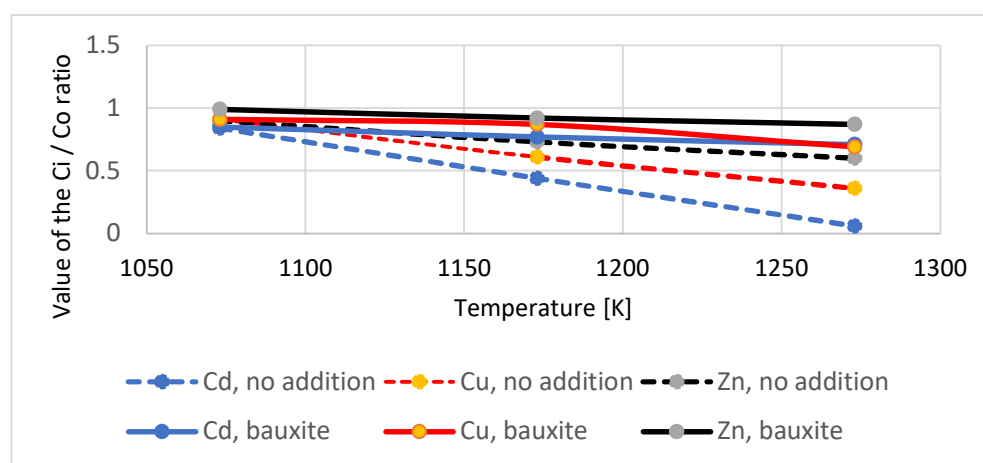
$$y = \frac{C_i}{C_0} = \frac{m_i}{m_0} \quad (1)$$

C_0 —metal concentration in the sample before roasting (in the input) [ppm_m]

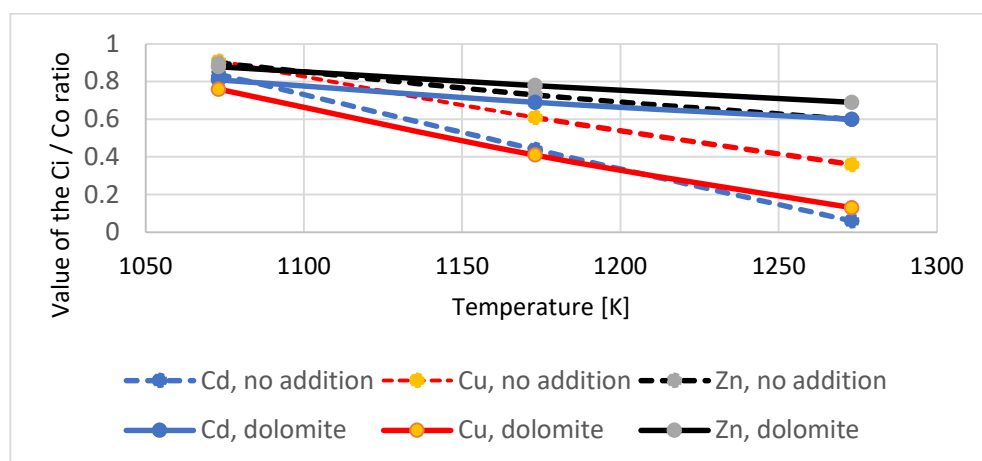
C_i —metal concentration in the test after ignition related to the input weight [ppm_m]

m_0 —amount of metal in the sample before roasting [μg]

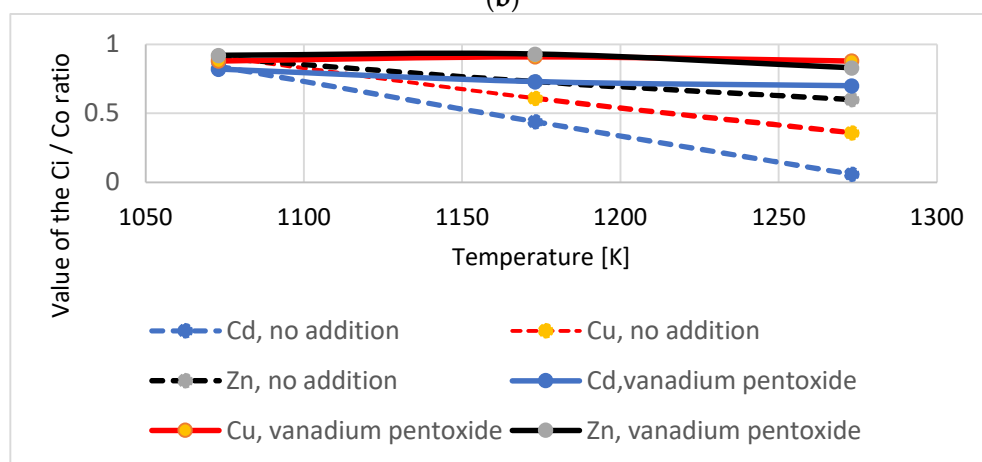
m_i —amount of metal in the test after ignition [μg]



(a)

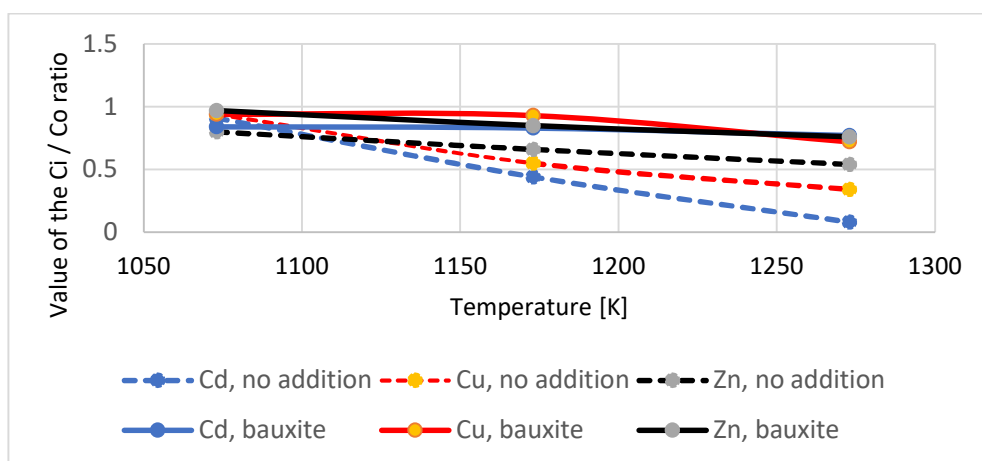


(b)

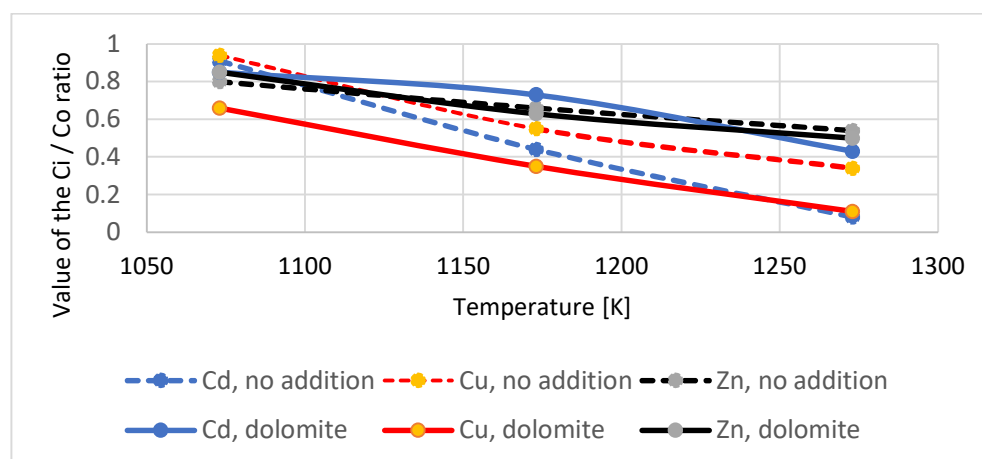


(c)

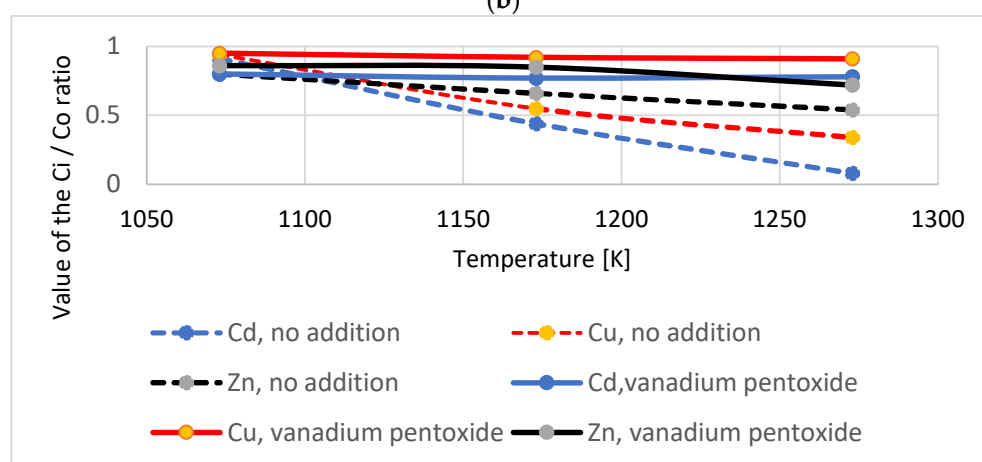
Figure 2. Dependence of the C_i / Co value on the roasting temperature in the samples of nitrates (V); (a) with the addition of bauxite, (b) with the addition of dolomite, (c) with the addition of V_2O_5 .



(a)

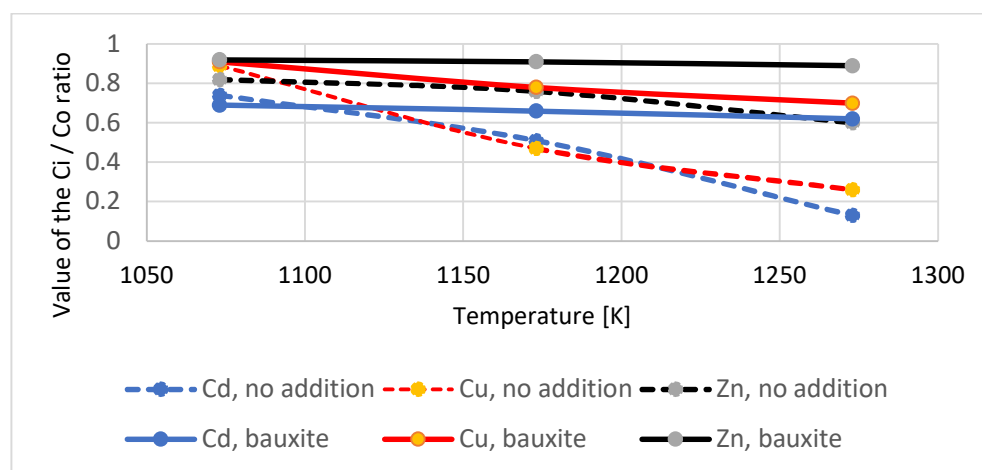


(b)

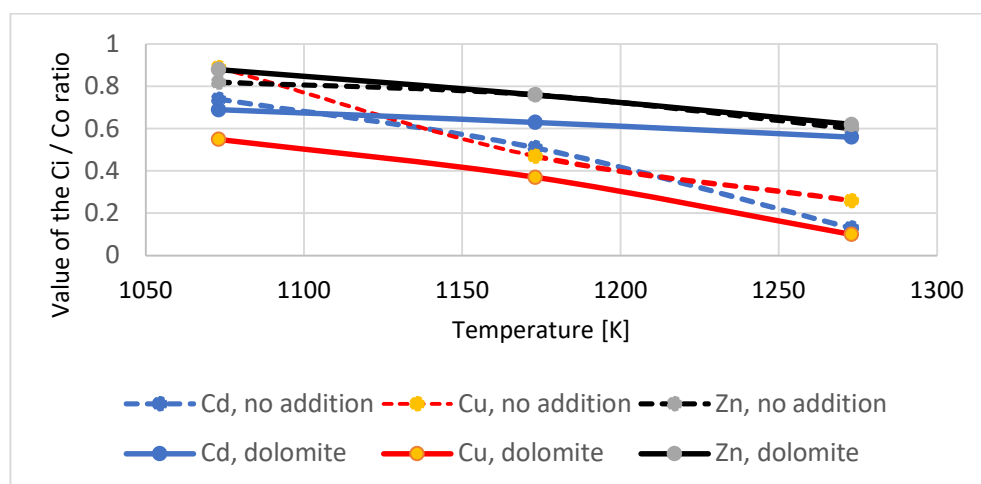


(c)

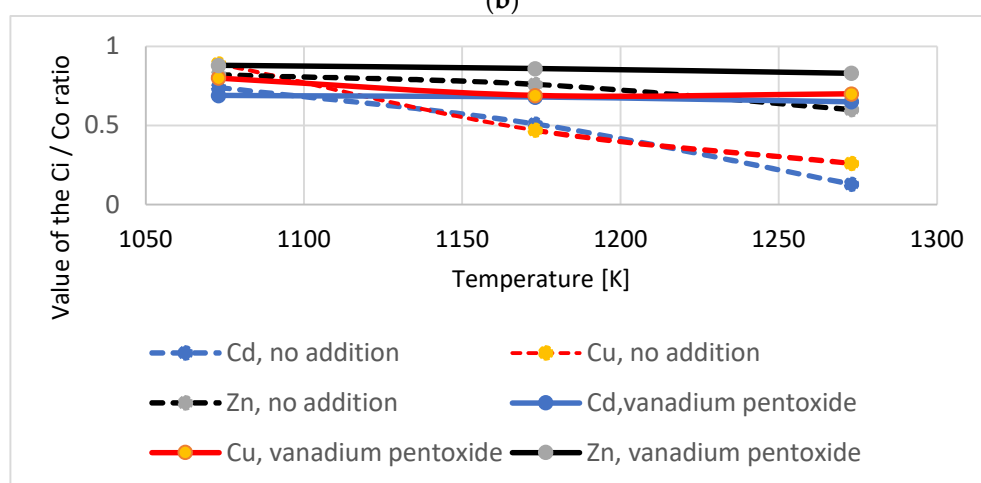
Figure 3. Dependence of C_i / Co value on roasting temperature in chloride samples); (a) with the addition of bauxite, (b) with the addition of dolomite, (c) with the addition of V_2O_5 .



(a)

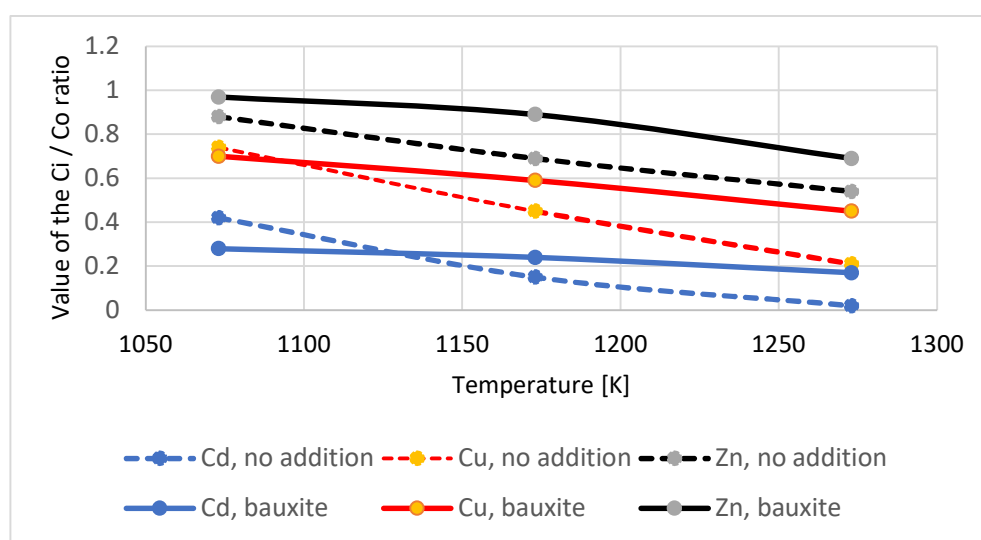


(b)



(c)

Figure 4. Dependence of C_i / Co value on roasting temperature in sulphate samples (VI); (a) with the addition of bauxite, (b) with the addition of dolomite, (c) with the addition of V_2O_5 .



(a)

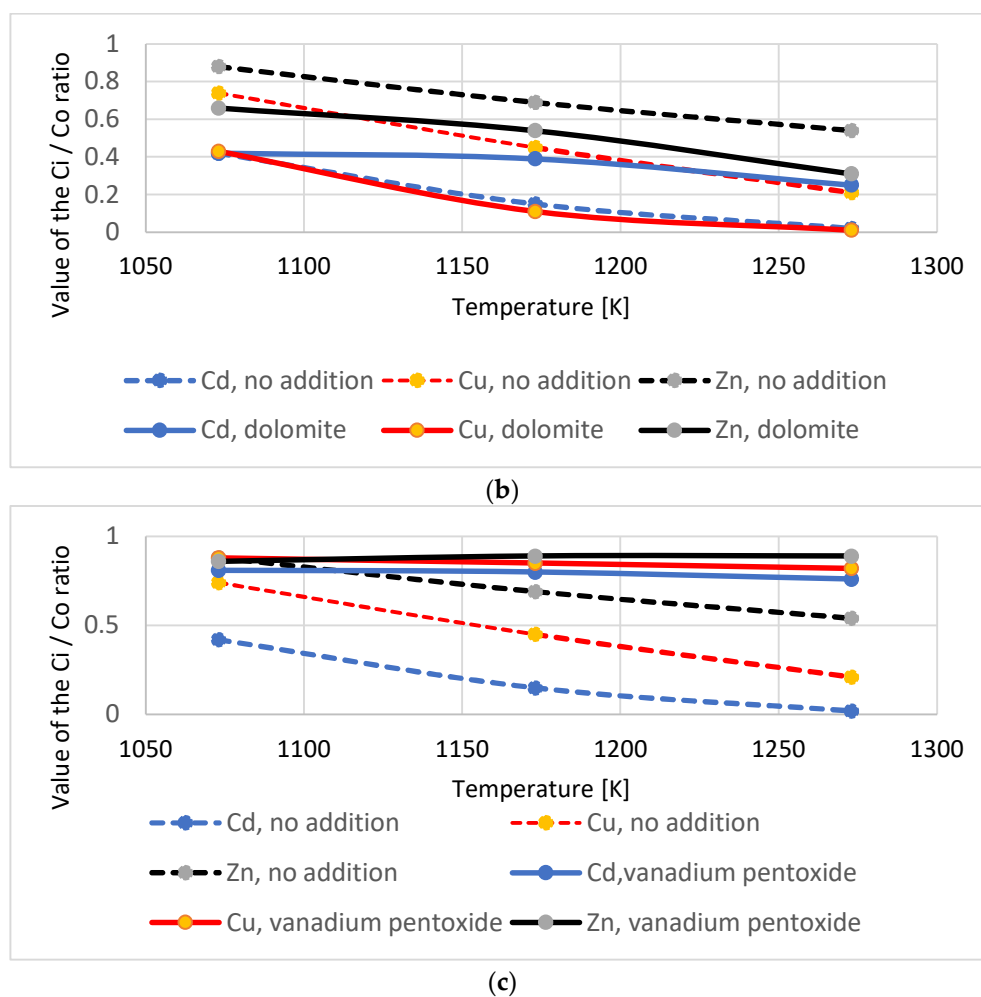
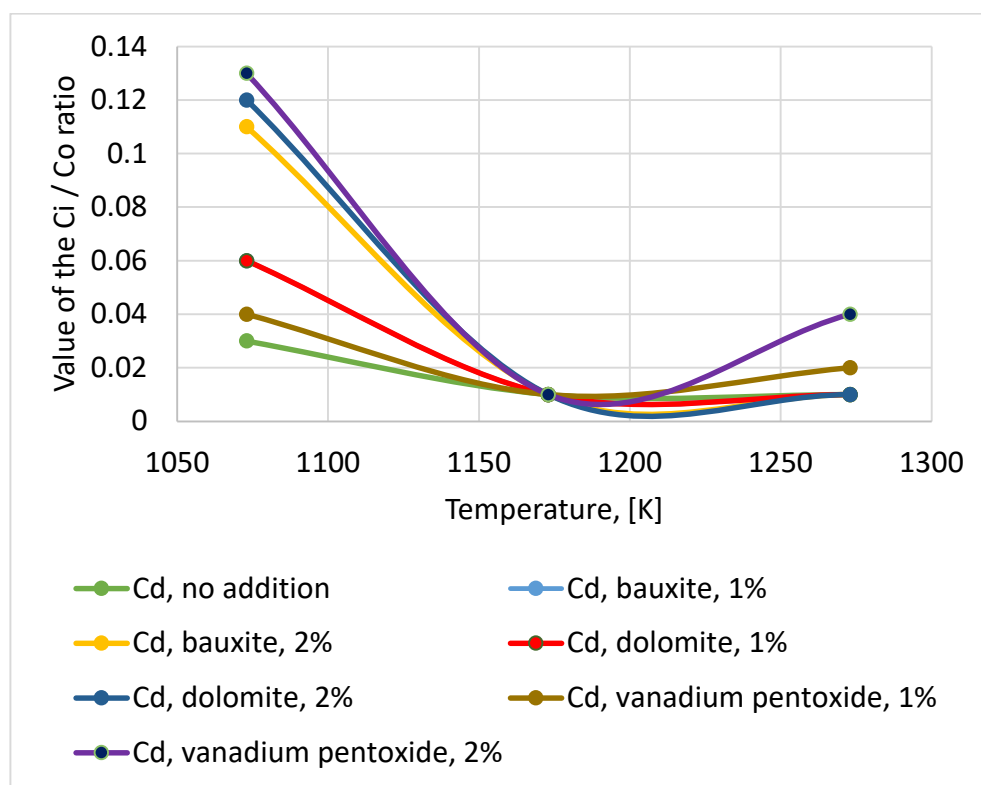
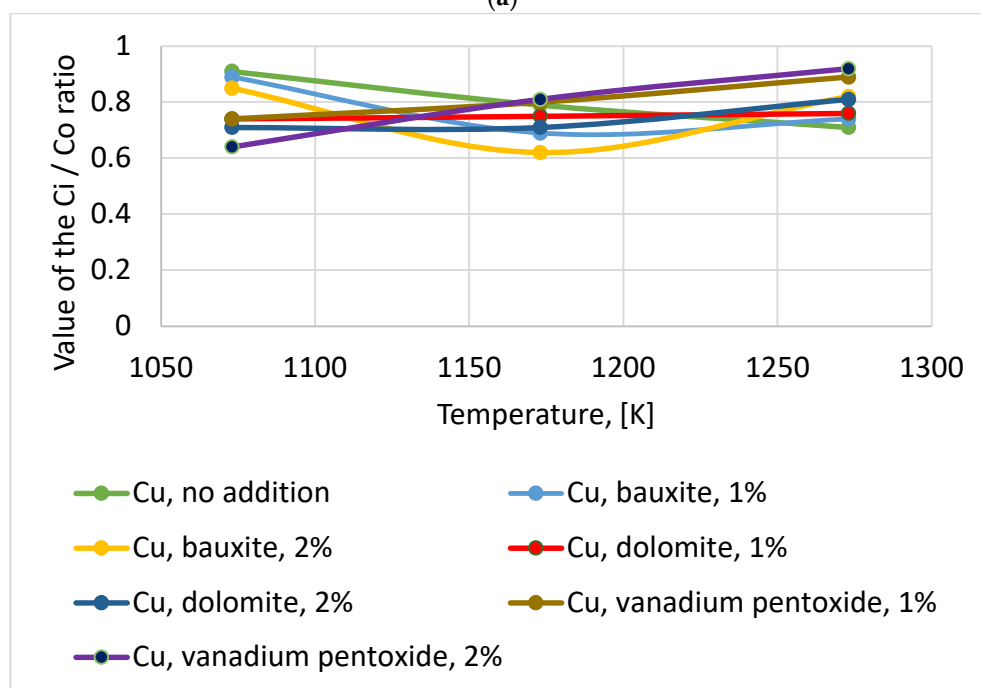


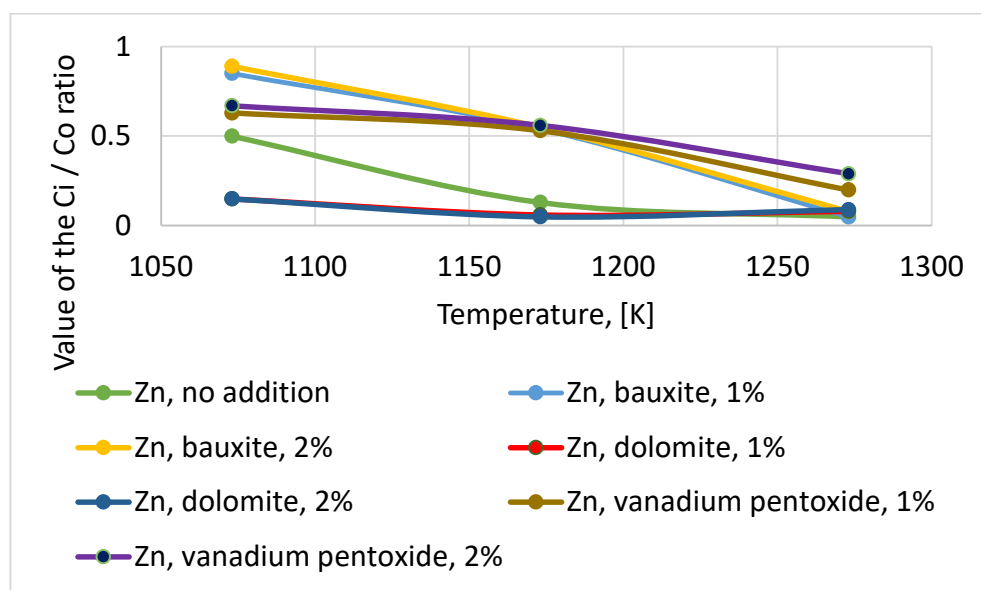
Figure 5. Dependence of C_i / C_o value on roasting temperature in samples of chloride mixture); (a) with the addition of bauxite, (b) with the addition of dolomite, (c) with the addition of V_2O_5 .



(a)

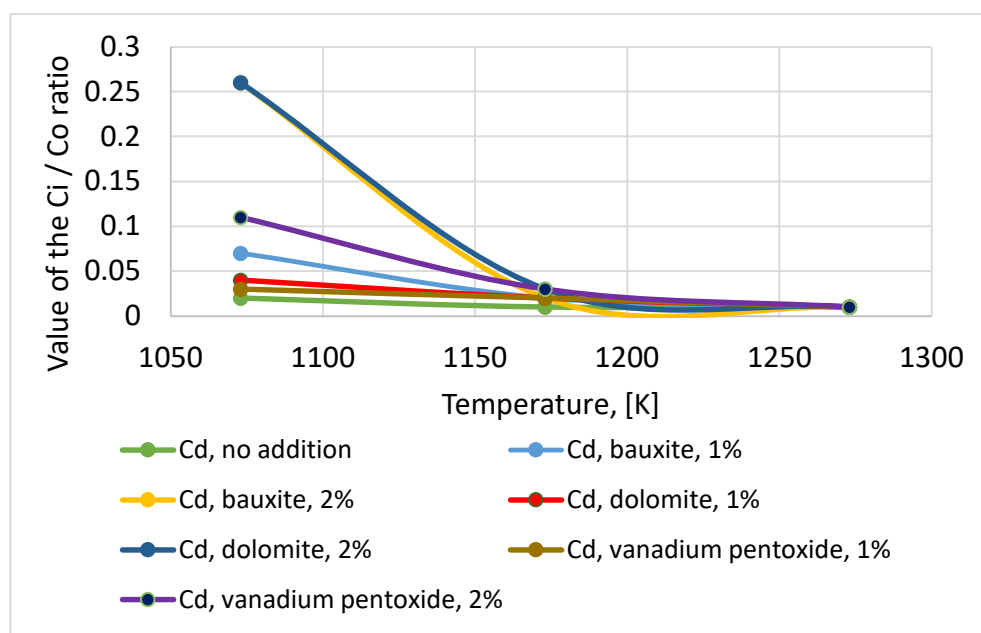


(b)



(c)

Figure 6. Dependence of the C_i/C_o value on the sewage sludge combustion temperature.



(a)

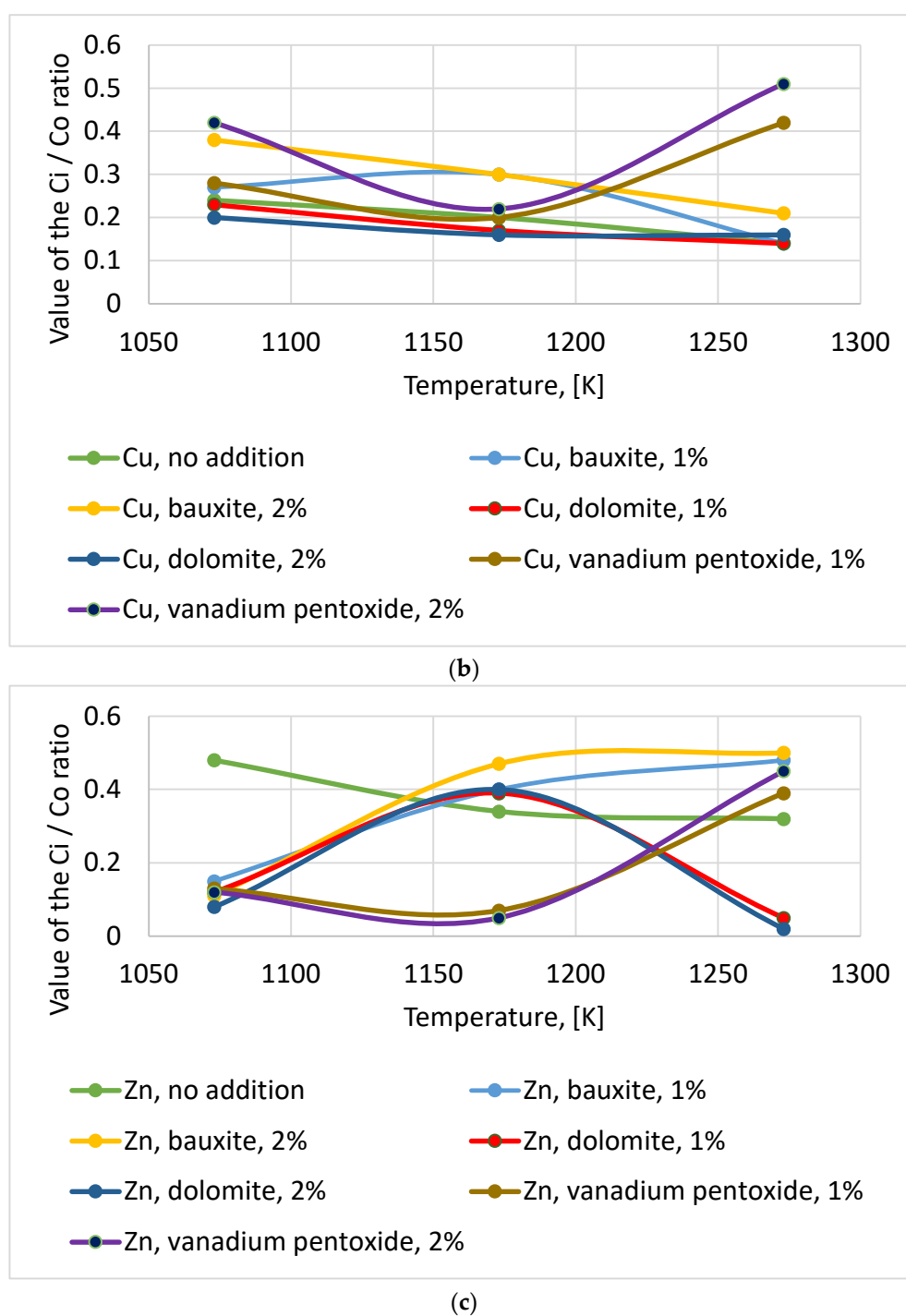
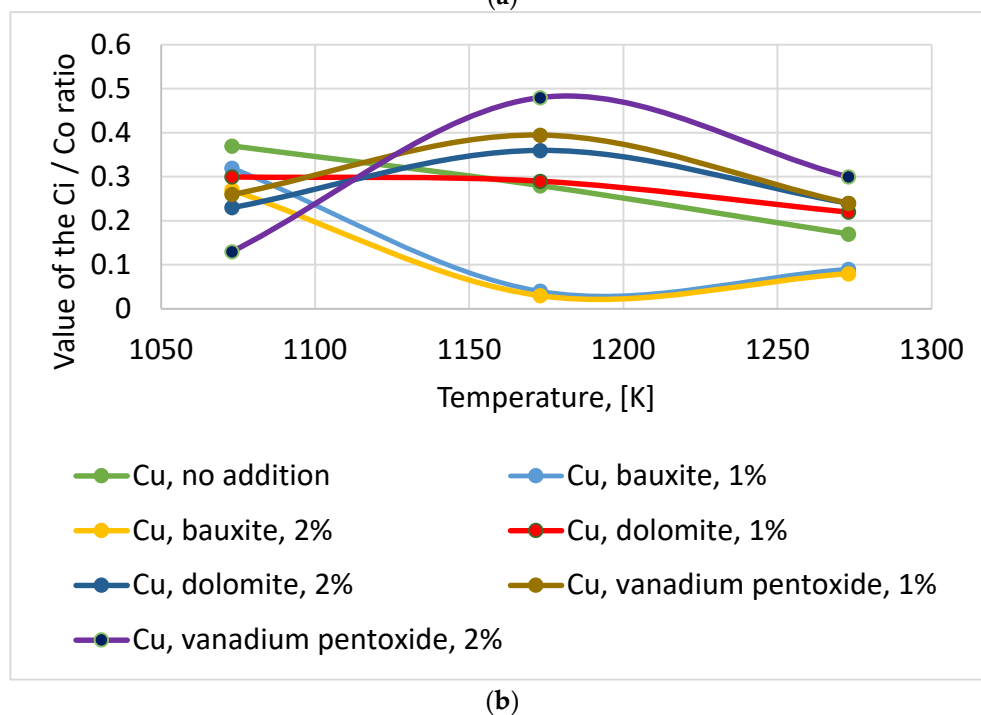
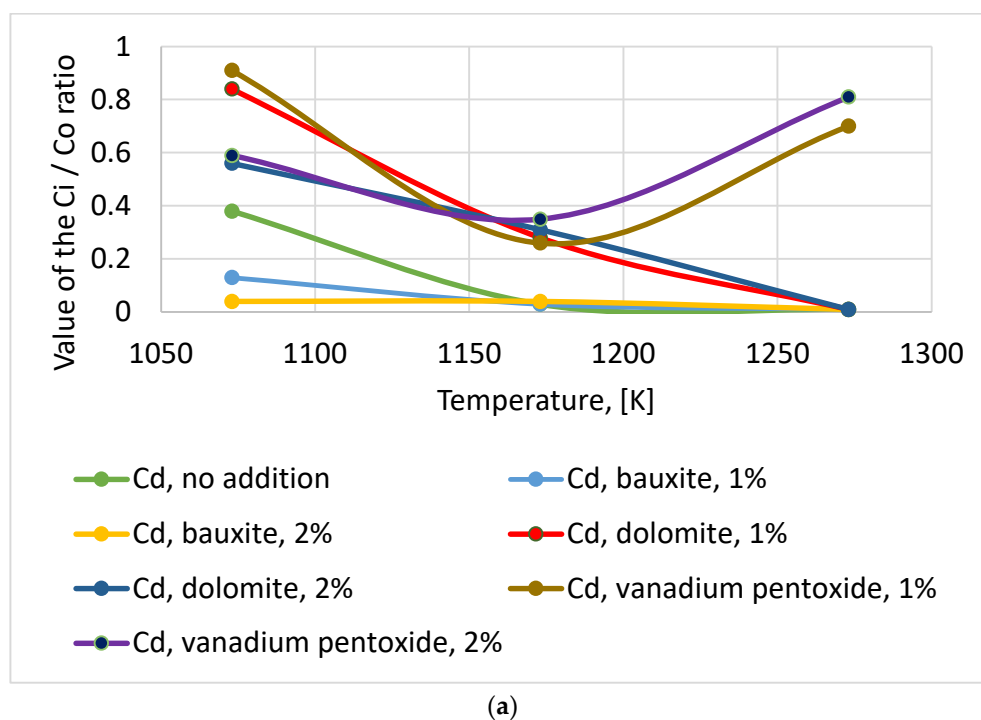


Figure 7. Dependence of the C_i/C_o value on the combustion temperature of rubber waste.



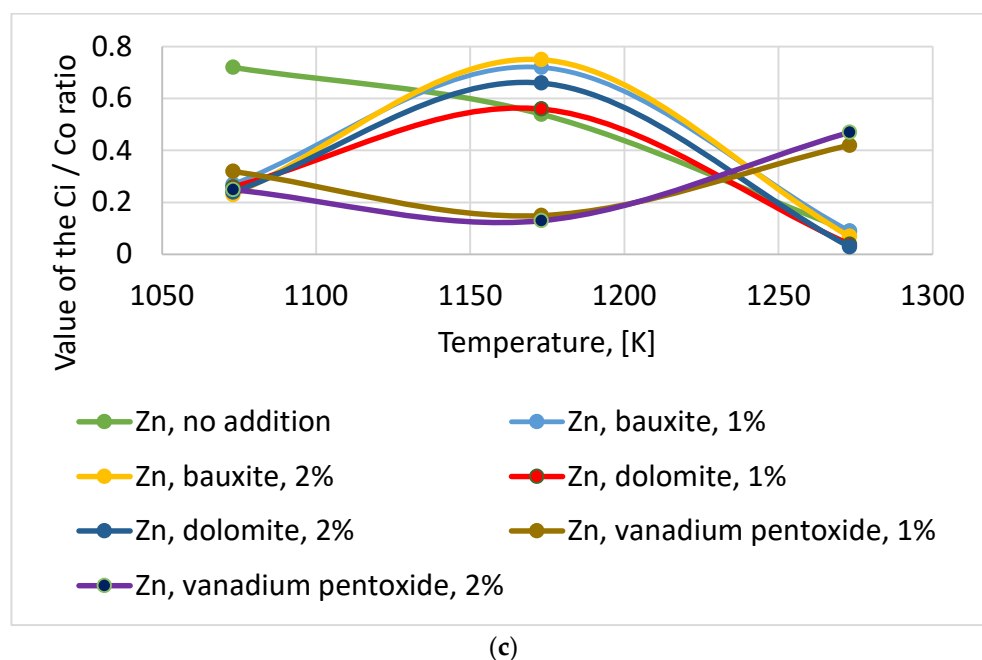


Figure 8. Dependence of the C_i/C_o value on the combustion temperature of fuel from SRF waste.

3.1. Results of Tests with Metal Salts

The initial concentrations of the metals Cd, Cu, Zn in the samples of their salts applied to the inert matrix (before roasting) ranged from ppm_m (CdNO₃)–570 ppm_m (CdCl₂). In the sample of all metal chloride mixtures, the amount of Cd was 546 ppm_m, Cu 467 ppm_m, and Zn 496 ppm_m (Table 1). During roasting, only a part of the initial amount remained in the solid residue, regardless of the initial form in which they were bound (nitrate (V), chloride or sulphate (VI)). It was found that metals at high temperatures 1073, 1173 and 1273 K partially evaporated and the higher the temperature, the higher the amounts (Figures 2–5). This process was dependent on the form in which the metal was present before roasting. In the sample after ignition at 1073 K, the amount of metals that remained was not drastically different from 74% Cd as sulphate and 84% Cd as nitrate and 80% Zn as chloride to 94% Cu as chloride. Burning metal salts at higher temperatures resulted in higher emissions to the gas space. The highest emissions were recorded at 1273 K. Therefore, for: Cd (NO₃) 94%, Cu (NO₃) 64%, Zn (NO₃) 40%, Cd (SO₄) 87%, Cu (SO₄) 74% Zn (SO₄) 40%, CdCl₂ 92%, CuCl₂ 66%, ZnCl₂ 46%.

The mutual interactions were observed in the samples containing the chloride mixture (Figure 5). It was different for the tested metals and for different temperatures. At the lowest temperature used, 1073 K, Cd emitted 58%, Cu 26%, and Zn 12%. On the other hand, at the temperature of 1273 K, the emissions increased—Cd 98%, Cu 79%, and Zn 46%.

Attempts were made to immobilize metals in the solid residue after ignition. Bauxite, which is a flux; dolomite, which has a sorption effect; and divanad pentoxide, which forms vanadates (thermally stable) at high temperatures, were used. Each of the additives lowered the emissions metals. Copper behaved differently during roasting with the addition of dolomite (regardless of the chemical form in which Cu was bound—Figures 3b, 4b and 5b). Its amount in the solid residue after ignition decreased. Cadmium (one of the most dangerous elements—a metal with a high bioaccumulation in the environment) was immobilized by all the tested additives, but copper was best affected by the divanad pentoxide. The highest values of immobilization of metals in the solid residue after ignition were obtained in samples with the addition of V₂O₅. For example, at the temperature of 1273 K, the addition of V₂O₅ caused the emission of Cd to drop to the level of 24%, Cu 18%, Zn 11%. Dolomite showed the lowest effectiveness. In general, dolomite did not have

a significant positive effect on the immobilization of metals, bauxite selectively, while divanad pentoxide gave a very good effect, retaining metals from 40–90% of their initial amount. Its binding effect is visible in the experiment with a mixture of chlorides (Figures 5a–c).

The authors found no information in the literature on studies with the use of metal salts.

3.2. Results after Waste Incineration

The results of the study of pure forms of metal salts were used in an experiment with three types of waste in which metals were contaminants. These wastes were neutralized by thermal means during high-temperature destruction. These amounts varied from a few mg Me/kg of waste (Cd in rubber waste and fuel from SRF waste) to several or several thousand mg per kilogram (zinc in sewage sludge—2791 mg and 17,095 mg in rubber waste).

By incinerating waste at temperatures of 1073, 1173 and 1273 K, the distribution of Cd, Cu and Zn present in the waste between the gas and solid phases was determined. The higher the temperature, the lower the amount of metals in the combustion residues. This is confirmed by the literature data [16–20]. Along with the flue gases, metals were removed from the furnace chamber after thermal decomposition of sewage sludge in amounts > 97% Cd (at the temperature of 1073, 1173, 1273 K), 95% Zn (1273 K), 87% Zn (1173 K), 50% Zn (1073 K). The lowest emission was related to Cu at 1073 K 8%, at 1173 and 1273 K, 21% and 29%. Cadmium also emitted >96% in the entire range of temperature tests, during the combustion of rubber waste as well as SRF fuel. After burning rubber waste, Zn was in the solid residue in the amount of 32% and 34%—temperature 1173 K and 1273 K, and 48%—temperature 1073 K. However, combustion of SRF fuel resulted in its emission at the level of 91% at the temperature of 1273 K and 54% and 72%, respectively, at 1173 and 1073 K. The amount of Cu after combustion of SRF fuel is: 37% (1073 K), 28% (1173 K), 17% (1273 K). However, after burning rubber waste, they were lower by 14% to 24%. The use of additives in the form of bauxite, dolomite or divanad pentoxide influenced the behavior of metals in waste incineration processes. This effect is illustrated in Figures 6a–c ÷ 8a–c. The effect of additives depended on the type of waste, type of metal and the furnace temperature. If the additive effectively retained metals, then their amounts in the ashes were higher by several to several dozen percent in relation to the amount in the ashes remaining after waste incineration without additives. None of the accessories turned out to be universal. Bauxite effectively reduced Zn emissions by 35–39% at 1073 K temperature during sewage sludge combustion and by ~20% at 1173 K temperature when SRF fuel was burned. In relation to Cd, bauxite (2%) increased its amount in the residue after burning rubber waste at 1073 K by 24%. The 2% addition of dolomite had a similar effect in this process. The possibilities of reducing heavy metal emissions with the use of sorbents: limestone, hydrated lime, bauxite and kaolinite were investigated in [20] by their injection into the furnace at temperatures of 1000 °C, 1150 °C and 1300 °C. Calcium additives (CaO , CaCO_3 , Ca(OH)_2), as heavy metal sorbents during the co-incineration of municipal waste (MSW) with sewage sludge, were used by the authors [21]. They found that these sorbents reduced the volatilization of Cu and Zn. The authors [7] also conducted research on the incineration of sludge with the addition of CaO . The addition of CaO inhibited the volatilization of Zn and Cu at temperatures up to 1000 °C. In [12], the use of Ca- and Si-based sorbents was proposed for the capture of Pb, Cd and Cr. When using divanad pentoxide as an admixture during the combustion of SRF fuel, a significant decrease in mobility was found: Cd by 53% at 1073 K, by 23–32% at 1173 K and by 70–80% at 1273 K; Zn by 33–38% at a temperature of 1273 K; Cu by 11–20% at a temperature of 1173 K and by 13% at a temperature of 1273 K. V_2O_5 also turned out to be effective in the immobilization of Cu contained in rubber waste. It lowered its emission at 1273 K from 86% to 28–37%. The emission of Zn during sewage sludge incineration with the use of V_2O_5 decreased at each of the tested temperatures: by 17% at the temperature

of 1073 K, by 43% at the temperature of 1273 K and by 24% at the temperature of 1273 K. The reports from the research presented in the literature show that the addition of V_2O_5 has not been used so far (apart from the research conducted by the authors of this study).

The tests used additives in the amounts of 1 and 2%. The effect of the amount of the additive in this case seems to be insignificant.

Calcium and other sorbents are often used in fuel and waste combustion studies as sorbents for heavy metal retention. The authors of the work [10] during the combustion of rubber and polyethylene waste used sorbents calcium $CaCO_3$ and calcium oxide CaO in order to capture heavy metals, e.g., Zn and Cu. They found that the efficiency of Zn scavenging by $CaCO_3$ increased with increasing temperature in the furnace. They also found that the sorption efficiency of $CaCO_3$ was worse than that of CaO . The research on the effectiveness of adsorption of various sorbents for heavy metals in various combustion conditions is presented in [22]. At the temperature of 800 °C, kaolinite and aluminum oxide showed the highest adsorption efficiency. Bauxite showed the best adsorption properties at 700 °C. The effectiveness of kaolinite—a sorbent for capturing heavy metals, including Cd, was also studied by the authors [19,23]. Their research has shown the advisability of using kaolinite to retain Cd at high temperatures of 1100–1200 °C [23]. The effect of sorbents (limestone, bauxite, calcium sulphate, calcium oxide, kaolinite) on heavy metal emissions under various combustion conditions is described in [24,25]. The increase in temperature was found to have a negative effect on the uptake of heavy metals by sorbents.

In the years 1996–1999, studies on the capture of ecotoxic metals in combustion processes were carried out at the University of Arizona [26]. For example, it was found that Pb reacted much faster with kaolinite than with hydrated lime. Cd, on the other hand, reacted faster with hydrated lime than with kaolinite. It was found that mixtures of hydrated lime sorbents mixed with kaolinite can be used to remove many toxic metals from combustion environments.

4. Conclusions

Research on the emissivity (at temperatures of 1073, 1173, 1273 K) of ecotoxic metals Cd, Cu, Zn bound in the form of salts—nitrates (V), chlorides or sulphates (VI)—showed that as the temperature increases, the metals gradually passed into the gas phase (regardless of the initial form in which they were bound). The highest emissions were recorded at 1273 K—Cd(NO_3) 94%, Cu(NO_3) 64%, Zn(NO_3) 40%, Cd(SO_4) 87%, Cu(SO_4) 74%, Zn(SO_4) 40%, CdCl₂ 92%, CuCl₂ 66%, ZnCl₂ 46%.

The additives used (bauxite, dolomite, divanad pentoxide), the effect of which at high temperatures were to reduce the transfer of metals to the gas phase, actually retained the metals in the ash. Their interaction was different for different metals. The highest values of immobilization of metals in the solid residue after ignition were obtained in samples with the addition of V_2O_5 , e.g., at the temperature of 1273 K, the emission of Cd decreased to the level of 24%, Cu 18%, Zn 11%. The Cd was immobilized by all additives. In relation to Cu, V_2O_5 turned out to be the most effective. Dolomite showed the lowest effectiveness.

During the combustion (at temperatures of 1073, 1173, 1273 K) of rubber wastes, sewage sludge and fuel from SRF wastes, the Cd, Cu, Zn metals contained in them partially passed into the gas phase. The temperature in the combustion chamber affects the emission capacity of metals. The higher the temperature, the higher the emission was. For example, if the temperature of the furnace in which each of the tested waste was burned was 1273 K, then the emission of Cd exceeded the value of 97%.

The additives retained metals in a solid residue after combustion with varying degrees of effectiveness. The decrease in Cd mobility by 70–80% in the temperature of 1273 K occurred when SRF fuel with the addition of V_2O_5 was burned. Bauxite effectively reduced the Zn emission by 35–39% in the temperature of 1073 K. None of the accessories turned out to be universal.

The transformation of metals during combustion and, thus, their mobility, is also influenced by the presence of elements in the combustible substance of the waste. For example, the presence of chlorine increases the possibility of volatile chloride formation and greater metal emissions.

The limitation in the research was the laboratory scale—the results obtained on the technical scale will certainly be interesting.

The obtained results induce the continuation and expansion of research in the field of:

- the mobility of other ecotoxic metals from incineration of other types of waste that must be disposed of by incineration,
- higher temperatures in the combustion chamber (because waste containing organochlorine compounds in terms of Cl > 1% must be incinerated at a temperature above 1373 K),
- the possibility of immobilizing these metals in the solid residue after incineration of waste (the use of the addition of V_2O_5 may give particularly promising results),
- the use of other additives of a different nature (reports in the literature usually concern sorbents),
- the scale of the experiment—tests on a quarter-technical scale and above.

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