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# Estimates of the influence of the solar irradiation spectrum energy on the intensity of heat treatment of solid waste with hexavalent chromium

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**Abstract.** Methods of processing chromium containing wastes are considered. Positive and negative aspects of widely used methods of transfer of hexavalent chromium to trivalent are indicated. It is proposed as the most effective way of thermal neutralizing of chromium-containing waste in a reducing environment. Field tests of samples containing hexavalent chromium and organic compounds, which showed the possibility of intensification of heat treatment processes using solar energy, were carried out. An estimation is obtained for the wavelength ranges of the near UV, the visible, and the near IR spectrum, within the limits of which photochemical reactions for the reduction of hexavalent chromium are possible. This will reduce the temperature of heat-treatment and, together with it, reduce energy consumption in heat treatment devices. The latter is also important for reducing greenhouse gas emissions.

**Keywords:** hexavalent chromium, solid waste, the electrical and electronic equipment, heat treatment, solar irradiation spectrum

## 1. Introduction

In 2002, the European Union introduced the original RoHS Directive (Restriction of Hazardous Substances), also known as Directive 2002/95 / EC, and in 2011, 2015, subsequent directives RoHS2, ROHS3 were published. After that, the use of hexavalent chromium (Cr VI) significantly decreased in the EU, as well as in many other countries. At the same time, we note that the directives impose restrictions on electrical and electronic products, while allowing the content of Cr VI in them to be 1000 ppm [1]. This is a significant number, as the stream of electronic wastes is growing rapidly in both developed and developing countries. For example, according to the Environment Directorate of the General European Commission ('DG Environment'), waste of electrical and electronic equipment (WEEE) such as computers, TV-sets, fridges and cell phones, is one, the fastest growing waste streams in the EU, with some 9 million tonnes generated in 2005, and are expected to grow to more than 12 million tonnes by 2020. Hence, such wastes can contain up to 20 thousand tonnes of Cr VI, which were used for anti-corrosion protection. It should also be borne in mind that hexavalent chromium compounds can be used in a number of other industries, for example, in tanning,



metalworking, or in painting processes, which are widely used in various spheres of production, including construction. Therefore, the problem while doesn't lose acuity, and the challenges of finding the best ways to Cr VI-containing waste processing remains to this day.

One of the possible ways of neutralizing hexavalent chromium compounds is to convert it to a less toxic trivalent or bivalent state. It can be carried out by various methods, among which currently used are mainly reagent, electrochemical, membrane, sorption and thermal methods. Each of them has its advantages, as well as general and specific imperfections. They are widely represented in the literature (see, for example, [2-8]), so we only note here that all methods are energy-consuming, and reagent and sorption methods are also material-consuming methods. Exceptions are the methods of membrane and heat treatment. At the same time, the membrane method requires preliminary purification of waste water from oils, surfactants, solvents, organics, and is characterized by the high cost of membranes. Therefore, as an optimal method, the method for neutralizing chromium-containing waste by heat treatment in a reducing medium of carbon monoxide is considered. CO as a fuel burnout product should be oxidized to carbon dioxide CO<sub>2</sub> with the reduction of Cr VI to Cr III and/or to Cr II.

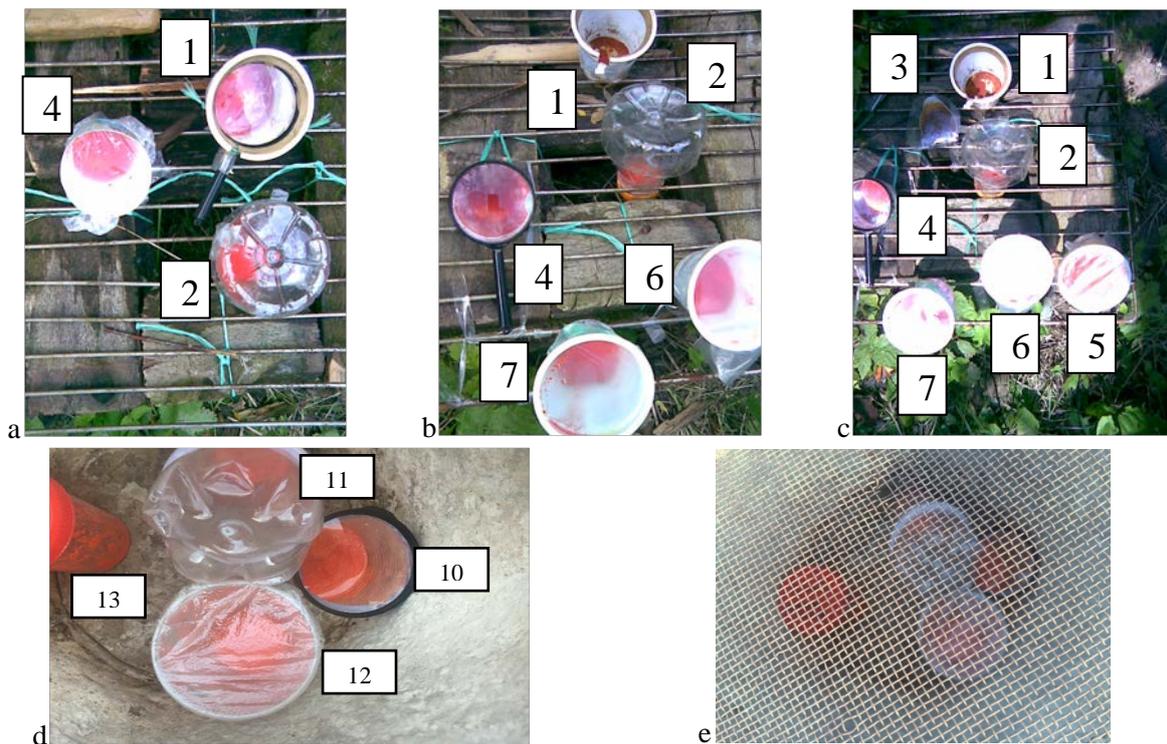
However, a lot of fuel is spent for heat treatment, since it is necessary to heat up to a temperature of about 700 °C and higher not only chromium, but the entire mass of waste. In addition, as we see, there is an inevitable output of carbon dioxide. Therefore, the creation of a heat treatment system that meets modern challenges, including the low-carbon requirements for the production and/or use of alternative energy sources, should aim to maximize the current reduction in energy consumption from carbon fuels. It is known that Cr VI in a mixture with organic compounds can be reduced at low temperatures if the mixture is exposed to solar or other radiation in the far and near ultraviolet (UV), and even in the visible part of the spectrum. So, for example, it is known that the canvases of artists of the 19th and 20th centuries, which used a lot of chrome yellow pigment in their works, under sunlight, and, perhaps, illuminated by daylight lamps, have now begun to acquire a greenish shade.

## 2. Methods

To determine the effect of photo-oxidation under solar irradiation on the efficiency of heat treatment of contained the Cr VI waste of coloring, field tests of the samples was carried out. Placement of samples at two experimental sites: in Kazan (latitude 55° 36', longitude 49° 19', altitude above sea level 128 m) and Naberezhnye Chelny (latitude 55° 42', longitude 52° 20', altitude above sea level 103 m), Russia, Republic of Tatarstan, is presented in Fig. 1, photo a, b, c, d, e. Geodetic heights at the location of samples in Kazan 102 m, in Naberezhnye Chelny 70 m.

The material for testing was K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> potassium dichromate of "chemically pure" class. The choice of material and class of purity was dictated primarily by the desire to ensure unambiguity and convenience of observation in the field conditions after a change in the state of the sample, which in this case can easily be done due to change of the sample color by the course of the experiment. 14/07/18 in Kazan, samples 1, 4 were installed in opaque white PET-beaker at a level of +0.250 m above the surface, with an inclination of the axis to the south by approximately 55° (Figure 1, photo a), which made it possible to irradiate the bottom of the beaker better when the sun is at the zenith. Sample 2 were installed vertically in a transparent PET bottle. In Naberezhnye Chelny, the samples were installed in transparent double beakers of polypropylene (PP) at a level of +2,800 m above the surface vertically. In Kazan, sample 1 was covered with a magnifying glass (an x6 loup), sample 2 – with a PET-plate, sample 4 - with a transparent polyethylene film PELD. Samples 6, 7 were placed 9 days later (Figure 1, photo b). Sample 6 was coated with a transparent no color PELD film, No. 7 with a transparent PELD film of pastel green color (Pastel Green, RGB 119 221 119, CMYK 46 0 46 13). Samples 6, 7 are also installed with an inclination of the axis to the south by approximately 55°. After 5 days, the samples 3, 5 (Figure 1, photo c) were installed (also with an inclination of the axis to the south of approximately 55°). The latter was prepared with natural drying oil. Sample 3 is covered with PET-plate, sample 5 – with PELD-film, both coatings are transparent and colorless. In the city of Naberezhnye Chelny on July 15, 2018 at 12:00, 4 samples 10, 11, 12, 13, were installed, mixed on drying oil oxol (Figure 1, photo d). Samples 11, 12 are covered with a colorless polyethylene

transparent film, sample 13 – with an opaque lid, sample 10 covered with a magnifying glass with a sixfold increase ( $\times 6$  loupe). To protect against accidental mechanical damage at a height of 0.5 m above the samples, a metal grid with  $3 \times 3$  mm cells is installed (Figure 1, photo e). Due to the magnifying glass it was possible to increase the layer temperature by an average of  $10^\circ\text{C}$ . In Naberezhnye Chelny on clear July days the layer temperature under the magnifier reached  $43^\circ\text{C}$ , in Kazan - up to  $46^\circ\text{C}$ . The temperature of the other samples was approximately equal to the ambient temperature. In addition to heating, the loup played the role of a filter on the range of the radiation spectrum incident on the samples within 300-6000 nm [9]. The transparency of the used polymer materials in the UV part of the spectrum is also small. In the near UV region in the interval  $\lambda = 200\text{-}400$  nm, the integrated light transmittance of a  $100\ \mu\text{m}$  PELD film is about 45%, in the visible part of the spectrum – 70% and in the IR part of the spectrum to  $\lambda = 2300$  nm – 80%. Approximately the same transmittance spectra in the UV and IR regions have PP: from 250 nm for thin films, or from 370 nm for thick (from 1 mm thick and thicker) to 2300 nm ([10]). However, PP is more transparent than PELD and has a transmission in both the visible and in the IR parts of the spectrum to 90%. According to [11], PET has a transmissive power in the visible and in the IR part of the spectrum up to 1500 nm, close to 90%. However, unlike PELD and PP, even a thin PET film ( $10\ \mu\text{m}$  thick) does not transmit radiation in the near UV region up to 320 nm, which is explained by the content in its molecular structure of the carbonyl group  $\text{C} = \text{O}$ , which is one of the types of chromophore groups [12]. Also, according to [11], the transmittance of PET drops to 10% in the far IR region at 1500 nm, and then has two transmission windows of 60-75% for the ranges 1500-3500 and 14000-19000 nm. Thus, the radiant energy incident on various samples was different in spectrum and intensity.



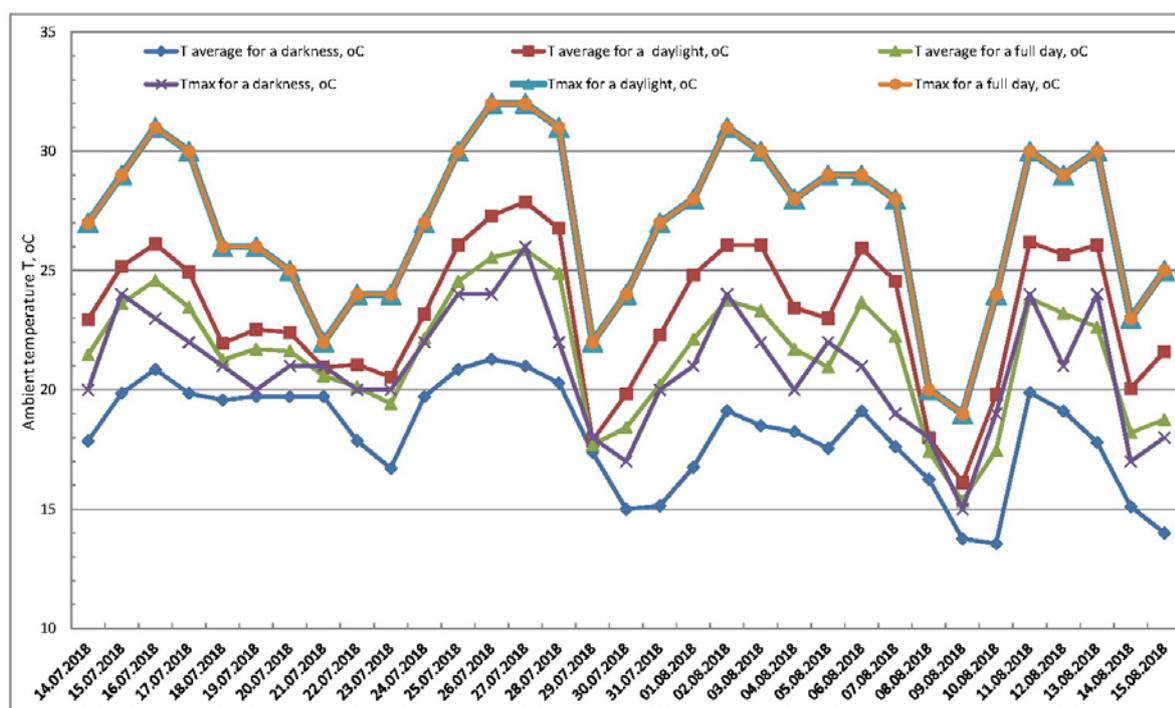
**Figure 1.** Installation and location of samples in Kazan (a, b, c) and Naberezhnye Chelny (d, e): a - 14/07/18; b - 23/07/18; c - 28/07/18; d, e - 15/07/18.

In the IR region of the spectrum, the irradiation conditions for samples 10, 11, 12, 13 were close to the irradiation of samples 5, 6 coated with a  $100\ \mu\text{m}$  PELD film, but 10, 11, 12, and 13 samples were irradiated 10% more intensively. For the PELD film from the transmission range of 200-400 nm in the

near-UV region, only the interval 345-400 nm is important for our tests, since the radiation in the 200-345 nm range is completely absorbed by the ozone layer of the atmosphere. Therefore, irradiation of samples 5, 6 under a colorless PELD film occurred in the range of 345-2300 nm, and a sample 7 under a 50 mm thick PELD film received the most intense irradiation in the visible spectrum at a wavelength of the order of 490 nm. Samples 2 and 3 under the PET plastic received energy comparable in intensity to PP in the range of 345-1500 nm (the interval 320-345 nm of the near UV region of the spectrum is absorbed by the ozone layer of the atmosphere).

### 3. Results and Discussion

Figure 2 shows the change of the outdoor temperature in Kazan. From these data it is clear that the daylight average temperature was lower of 20°C during 3 days, and the daylight maximum temperature 30°C and higher fixed during 10 among 32 of test days. The icons in Figure 2 allow you to distinguish between types of temperature during the day. Here the maximum and average temperature was prepared for darkness, daylight and a full day.



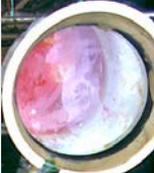
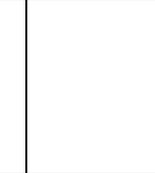
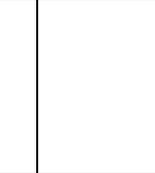
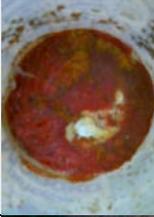
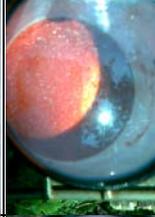
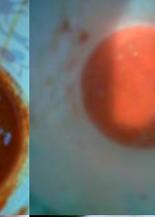
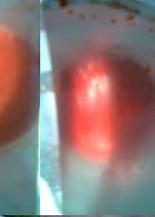
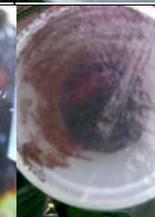
**Figure 2.** Graph of outdoor temperature for the period of field tests from 14/07/18 to 15/08/18 in Kazan.

The photographs in Table 1 show the change in the state of samples 1-7 from 16/07/18 to 15/08/18. The results of the test showed that the photochemical effect is manifested on the surfaces of all the samples. The most intensive changes occurred in the samples 1, 4 on the drying oil "Oxol" and 3, 5 on natural drying oil, and least intensively - in sample 2 on the drying oil "Oxol". Sample 1 for 1 week was covered with a magnifying glass, and sample 4 - with a no color PELD film. The remaining time the sample 1 stood open, and PELD-coating of sample 4 was replaced by a magnifying glass. The increased transformation of the material surface in samples 1, 4 can be explained by an increased sample temperature, exposure to atmospheric moisture (after the formation of the film), and a longer exposure to solar radiation. Sample 3 was coated with a 400  $\mu\text{m}$  thick PET-plate, and sample 5 - with a colorless PELD film 100  $\mu\text{m}$  thick. The next day after installing the samples, a dark film of drying oil formed on their surfaces. The film of the material on the walls of the beaker acquired a light brown

color. In samples 3, 5 the material with the original color of potassium dichromate were not observed. The change in the state of samples 3, 5 indicates a photochemical effect not only and not so much on the pigment as on the film-forming material, with the acceleration of oxidative processes in it. The further extension of these processes into the depth of layer occurs by a chain mechanism. The high intensity of the process in samples 3, 5 also indicates a better proceeding of reactions in them when using natural drying oil, in comparison with the drying oil "Oxol".

The sample 2 in the PET bottle was installed vertically and had the poor geometric conditions of irradiation. Despite the length of testing, its material was transformed only in the form of separate blackening zones of the upper layer, but the underlying layers, after sampling of part of materials on 15/08/18, retained their original color. Consequently, the presence of irradiation in the range of 345-400 nm of the near UV spectral region in sample 2 did not provide the intensification of the process.

**Table 1.** Change in the state of some samples during the tests due to solar radiation.

Dates	Sample Numbers						
	1	2	3	4	5	6	7
16/07/18							
23/07/18							
28/07/18							
03/08/18							
13/08/18							

In samples 6 and 7, the changes occurred at an average rate and, in comparison with sample 2, were expressed in a much more (some of twice in the time) intensity formation of the blackening areas of the surface and the acquisition of a red - cherry color of the subsequent layer. At the same time, the

lower layers, adjacent to the bottom of the beaker, retained the original color in both samples. During the tests the water didn't go into samples. We can also see that in sample 7, coated with a 50 micron PELD color film, the processes were more intensive than in sample 6 covered with a non-colored PELD film 100 microns thick. Hence, irradiation in the range of 345-400 nm in the Near-UV spectrum and in the interval of 700 -2000 nm in the Near-IR spectrum didn't give the advantage to sample 6.

A photometric analysis of samples at a wavelength of 540 nm was performed in accordance with GOST 31956-2012, method A, which corresponds to ISO 18412:2005, "Water quality – Determination of chromium (VI) – Photometric method for weakly contaminated water". The analysis was carried out with the UNICO SQ-2800 model spectrophotometer that permits the work operation in the wavelength range of 190 nm to 1100 nm, and is supplied of a dot matrix LCD display for photometric results. The correlation coefficient of the calibration graph was 0.9993.

The results of photometric analysis in the main corresponded to the results of the visual observations presented above. The greatest transition of hexavalent chromium to the trivalent and the divalent state occurred in samples 1 and 4–18% and 17%, respectively. Transformations in samples 3, 5 on natural drying oil – 16% and 4% are also noticeable. At the same time, in sample 7, in spite of significant visual changes, the hexavalent state of chromium was changed only by 1%. This fact can be explained by the fact that under the conditions of sample 7, an intensive conversion of dichromate to hexavalent chromate of potassium, having a black color, took place. The photometry also showed changes close to zero in sample 6. The latter does not contradict visual observations. At the same time, unexpectedly high result (about 35%) was fixed at sample 2 that visually almost has unchanged. The latter can only be explained by the error in sampling in the field conditions, in connection with which this result is recognized as not significant. It should also be noted that photometry with high accuracy, corresponding to the used model of the spectrophotometer, was hampered by the presence of organic substances and, possibly, a desiccant in the sample. Therefore, the analysis can be regarded as semi-quantitative.

#### 4. Conclusions

Thus, the carried out investigations have shown the possibility of intensifying heat treatment of waste containing hexavalent chromium and organic compounds using solar energy. An estimate is obtained for the wavelength ranges of the near UV spectrum, the visible spectrum and the near IR spectrum, within the limits of which photochemical reactions for the reduction of hexavalent chromium are possible. This will reduce the temperature of the heat-setting process and, together with it, reduce energy consumption in heat treatment devices. The latter is also important for reducing greenhouse gas emissions.

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