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Remediation Efficiency of the In Situ Vitrification Method at an Unidentified-Waste and Groundwater Treatment Site

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Abstract: The subject of this study was the dust collected from an electric arc furnace at an unidentified-waste treatment site in southern Taiwan. The dust underwent an in situ vitrification (ISV) process and was tested using the toxicity characteristic leaching procedure (TCLP), at the end of which the final product was analyzed for its stability and weather resistance. This study then examined the above results to determine whether the ISV process helps to enhance the efficiency and economic benefits of said waste-treatment site. A TCLP test conducted on the dust that had been treated with ISV revealed that concentrations of various heavy metals were not only far below those of the unprocessed sample dust but also fell below the limit stipulated in the TCLP regulation of Taiwan's Environmental Protection Administration. The results show that after undergoing ISV treatment, heavy metals in the dust were either encapsulated or bound in silicon lattices and thus barely leached from the dust. Analyses using scanning electron microscopy (SEM) and an energy dispersive spectrometry (EDS) indicate that the surface of the dust appeared more compacted after going through the ISV process. In addition, the highly contaminated dust that underwent ISV treatment saw a pronounced decrease in or elimination of wave crests. Another analysis applying X-ray diffraction (XRD) showed that the SiO_2 crests disappeared in the processed dust, suggesting that the crystal structure was replaced with quasi-vitreous products after ISV treatment. In the event that pollutants were extant, they were usually characterized by smaller size, high stability, excellent weather resistance, an innocuous nature, and recyclability.

Keywords: in situ vitrification; TCLP; electric arc furnace; dust

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1. Introduction

Taiwan is witnessing the maturation of waste treatment as regulations and prevention measures are being optimized. Nevertheless, illicit operations occur from time to time, and some companies fail to undertake their social responsibility, operating illegally or commissioning waste treatment to other parties at a low price. Such action takes a great toll on the environment. Waste from unidentified sources mentioned above is known collectively as "unidentified waste" [1,2]. A large part of unidentified waste is harmful to the environment. It often end up contaminating nearby underground water and soil in the proximity and jeopardizing people's health as it disseminates out from waste-treatment sites through osmosis or runoff. The situation illustrated above points to the need for appropriate and effective remediation schemes for waste-treatment sites. Waste-treatment technologies currently adopted include incineration and solidification [3]. More specifically, solidification can be further categorized into cement-based solidification, lime-based solidification, thermoplastic-based solidification, polyrock-based solidification, surface encapsulation, and in situ vitrification (ISV) [4].

ISV is both a kind of heat treatment and in situ solidification/stabilization technique. It works by sending high-voltage electricity flows through electrodes inserted in the soil, resulting in high temperatures (1600–2000 °C) that melt the soil, trap metal contaminants (soil or vitreous materials) in the soil, and cause organic pollutants to pyrolyze. The ISV process was first developed by the Pacific Northwest National Laboratory of Battelle Memorial Institute in 1980 for treatment of transuranic radioactive waste [5]. Years of trial and error proved that the ISV technology could treat waste, such as contaminated soil, dewatered sludge, slag, alluvial deposit, and asbestos [6,7]. ISV technology helps turn inimical organic materials into innocuous water vapor, carbon dioxide, or gases of simple composition. It also renders cooled slag into a solid glass-like material with a dense and impermeable surface that hinders harmful elements from leaking [4,8,9]. Therefore, from a technical viewpoint, melted treatment is highly applicable to the treatment of waste with high heavy metal content. For instance, sewage sludge can be rendered harmless by melted treatment and vitrification, while the residuals can be made into construction materials for buildings or roads [10,11]. In addition, ashes produced from incineration of municipal waste can also undergo melted treatment and vitrification, which trap heavy metals in the ashes, preventing them from dissolving in water, and cutting down the volume of ashes, thereby extending the lifecycle of landfills. Furthermore, ISV technology reduces the waste volume by 20% to 50% and purifies the surface of the waste, which, when coupled with melted treatment that gives the waste a dense surface and high weather resistance, can turn waste into reusable materials [12,13].

Currently, there are hazardous waste-contaminated sites in Taiwan, many of which are listed as contaminated sites that need to be immediately cleaned up. However, there is no place to store hazardous waste after it is excavated. Moreover, said waste may turn into secondary pollutants. The effects of infiltration and runoff processes on hazardous-waste disposal sites often result in the leakage of leachate. Such leakage further causes severe groundwater and soil contamination near the sites, which is harmful to ecological environments and human health. Thus, proper and effective strategies have been sought for remediation of contaminated sites. This study aims to apply in situ vitrification (ISV) technology in the remediation of unidentified-waste treatment sites, with electric-arc-furnace dust collected from an unidentified waste-disposal site in southern Taiwan as its subject. The physicochemical properties of the sample before and after undergoing the vitrification process, as well as the TCLP test on pollutants, were analyzed to determine the stability of the final product. Moreover, various instruments were used to prove the final product's physical properties. These results were then used to evaluate the effectiveness and economic benefits of vitrification.

2. Materials and Methods

2.1. The Source of the Samples

The sources and composition of unidentified waste of treatment sites are complicated. Therefore, this study looked into dust collected from an electric arc furnace at a waste-treatment site in southern Taiwan. A physiochemical analysis was also conducted on samples before and after the ISV process; the results were compared to evaluate the effectiveness of the ISV treatment.

2.2. The ISV Process

The ISV process was as follows: (1) Insert four equally spaced molybdenum/graphite electrodes to the appropriate depth in the area to be treated. Then, spread a layer of conductive material (graphite chips, glass frit, silica sand, or a mixture thereof) among the four electrodes as a catalytic promoter. (2) Heat is generated when the electric current passes through the catalytic promoter, and the soil starts to melt. At a temperature of approximately 1600–2000 °C, the melting expands downwards and outwards. The soil is electrically conductive when it has become molten and therefore continues its melting process until the required depth is reached. (3) When the required depth is reached, immediately cut the electric supply and withdraw the electrodes. Molten soil will cool down and solidify in the natural environment. (4) Cover the molten soil with clean soil, and the process is complete. To simulate the in situ environment when doing an ISV process, evacuate a circular hole of 80 cm in diameter and 40 cm in depth and place the sample dust into the hole. The process should be operated in open air; therefore, it is inoperable in case of rain or muddy ground.

2.3. Basic Component Analysis of the Dust

This study adopted the acid digestion method [14] to measure the amounts of oxides, such as Si, Al, Fe, Na, K, C, Mn, and Mg, and heavy metals, including Pb, Cu, Zn, Cd, Zn, Cr As, Hg, by using the filtrate of the dust to induce the inductively coupled plasma atomic emission spectrometer (ICP).

2.4. TCLP of the Dust before and after ISV Treatment

Pre- and post-ISV samples were analyzed via the TCLP test in order to compare the amounts of leaching before and after the ISV process and the effects of stabilization after solidification.

2.5. SEM and EDS Analyses of the Dust before and after ISV Treatment

The main component of the field emission scanning electron microscopy (FESEM) used in this study is the JEOL JSM-640 (JEOL Ltd., Tokyo, Japan) secondary electron detector. To avoid hitting residual gas molecules on the surface of the sample under electron beam irradiation, the SEM must be maintained at 10^{-4}–10^{-6} torr. SEMs are widely applied for various purposes. When combined with an energy dispersive spectrometer (EDS), an SEM can be used for qualitative, quantitative, point, and line analyses, as well as mapping. An SEM was used in this experiment to observe the surface-structure changes of the dust. An EDS was used to observe the elemental distribution in the dust structure and its properties.

2.6. X-Ray Diffraction Analysis (XRD Analysis) of the Collecteion Dust before and after ISV Treatment

Change in crystal structure could serve as a key indicator of successful vitrification. XRD analysis conducted using an X-ray diffractometer (Rigaku RINT-2000) (Rigaku Ltd., Austin, Texas, TX, USA) With CuKa as the light source, analysis of the crystal patterns of the dust was performed to learn the spacing of layers of materials. The X-ray wavelength produced was 1.5418 $\AA$; the operating current during testing was 10 mA; the voltage was 20 kV; the scanning speed was 5 deg/min; and the scanning angle was 2θ = 2–40°.

3. Results and Discussion

3.1. Physicochemical Analysis of the Dust

Table 1 exhibits the physicochemical properties of the dust before the ISV treatment; Figure 1 shows the exterior of the dust before and after the ISV process. Table 1 demonstrates the dust as a strong alkali with a pH value of 11.68, which was contributed by the electric arc-melting process in a steel mill in southern Taiwan, where the dust was collected. During the process, heavy metals and other elements in the molten steel evaporated into gas and then reacted with oxygen in the electric arc furnace to condense solid particles [15]; the heavy metal components were collected and became part of the dust. As a result, these particles were rich in alkaline substances, accounting for the dust's high pH values. Moreover, Table 1 shows that the metal oxides in the dust are mainly SiO_2 and Fe_2O_3, which corroborates the results of Inagaki and Kang's research [16]. There were high concentrations of heavy metals in the dust, such as Pb, Cu, Zn, and Cr, as shown in Table 1. During the electric-arc-furnace steelmaking process, the steel mill recycled scrap iron and steel; through the high temperature of the electric arc furnace, they melt to make steel [3]. In the steelmaking process, the suspended particles and gas emissions were part of the dust. The raw materials for steelmaking come mostly from imported scrap iron and metal, so the dust is rich in various heavy metals [17]. Figure 1 shows that the dust has a reddish-brown color before the ISV process; it appears grey and crystalline after the ISV process, as well as appearing hardened. It is suggested that the dust can be reused, for example, for road gradation or engineering structures [7,18].

Table 1. Analysis of the basic physiochemical properties of the dust.

Analysis Item \ Name of Sample	Dust (Not Undergoing the ISV Treatment)
pH	11.68
Oxides (wt%)	
SiO_2	48.05
Al_2O_3	1.65
Fe_2O_3	37.04
Na_2O	ND < 0.36
K_2O	1.54
CaO	6.07
MnO	2.39
MgO	3.24
Heavy metals (mg/kg)	
Pb	10,100
Cu	2725
Zn	203,500
Cd	272
Ni	267
Cr	1220
As	20.73
Hg	ND < 3.5

Note: in the table, "ND" means below the detection limit.

(**a**) (**b**)

Figure 1. Exterior of the dust before (**a**) and after (**b**) ISV treatment.

3.2. TCLP Analysis Results of the Dust before and after ISV Treatment

This study conducted the TCLP test to determine whether the dust was hazardous after ISV treatment. Table 2 shows the TCLP results of the dust before and after ISV treatment. According to Table 2, the concentrations of all heavy metals in the processed dust fell below the limit stipulated in the regulation of Taiwan's Environmental Protection Administration. Such a result demonstrates that although the dust was rich in heavy metals, heavy metal concentrations could be significantly reduced by carefully controlling the temperature and length of the ISV treatment, as well as proper application of the catalytic promoter during the process [4,6,9]. The same result also indicated that after undergoing ISV treatment, heavy metals in the dust were either encapsulated or bound in silicon lattices and thus barely leached from the dust [4,15], which is why the highly contaminated dust had low TCLP concentrations.

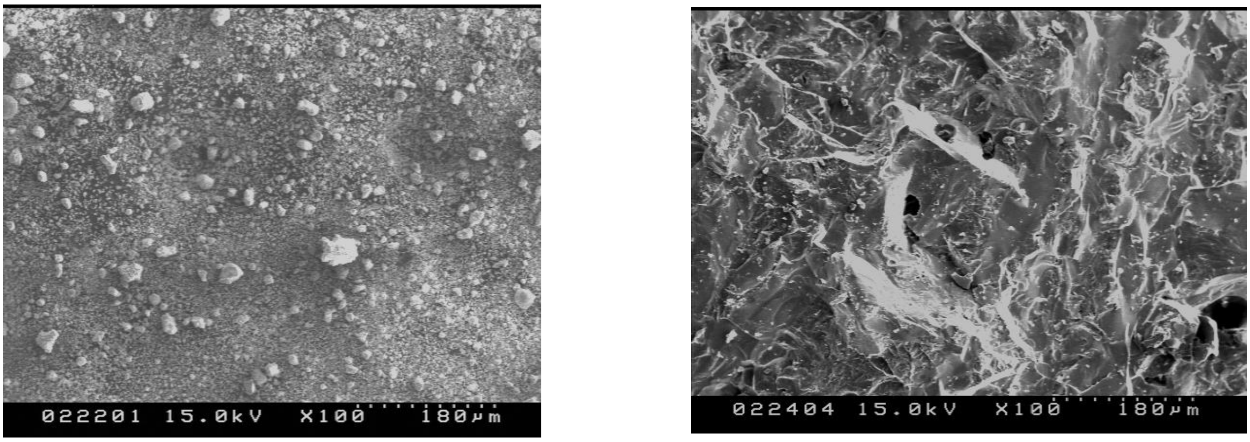
Table 2. TCLP results of the dust before and after ISV treatment.

Analysis Item \ Name of Sample	Dust		Regulatory Standard (mg/L)
	before ISV Treatment	after ISV Treatment	
	mg/L		
Pb	246.50	2.58	5.00
Cu	11.87	0.83	15.00
Zn	1525.50	102.50	-
Cd	57.36	0.12	1.00
Ni	2.05	ND < 0.14	-
Cr	0.54	ND < 0.078	2.50
Zn	0.11	ND < 0.005	5.00
Hg	ND < 0.0001	ND < 0.0001	0.20

Note: in the table, "ND" means below the detection limit.

3.3. SEM and EDS Analysis Results of the Dust before and after ISV Treatment

Figure 2 shows the SEM analysis results of the dust before and after ISV treatment. According to Figure 2, the surface of the dust appeared more compacted after undergoing the ISV process. Such a result corresponds to the studies of Gong et al. [19] and Pisciella et al. [5], which suggested that melting the waste could turn all hazardous substances into innocuous vapor and carbon dioxide. Furthermore, the melted ash became vitreous solids after cooling down, making the surface more compacted and impervious to hazardous substances [20]. Figure 3 shows the results of EDS analysis of the dust before and after ISV treatment, suggesting that after undergoing the ISV treatment, the highly contaminated dust experienced a pronounced decrease in or elimination of wave crests [4]. This result corresponds to that mentioned in Section 3.2, i.e., heavy metals in the dust were either encapsulated or bound in silicon lattices after ISV treatment and thus barely leached from the dust [4,9].

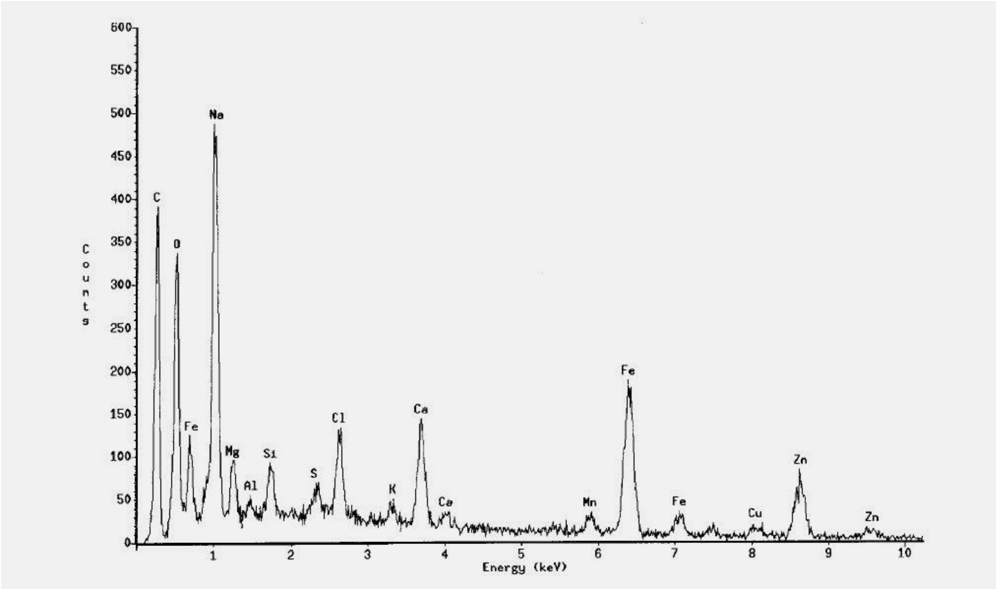


(**a**) (**b**)

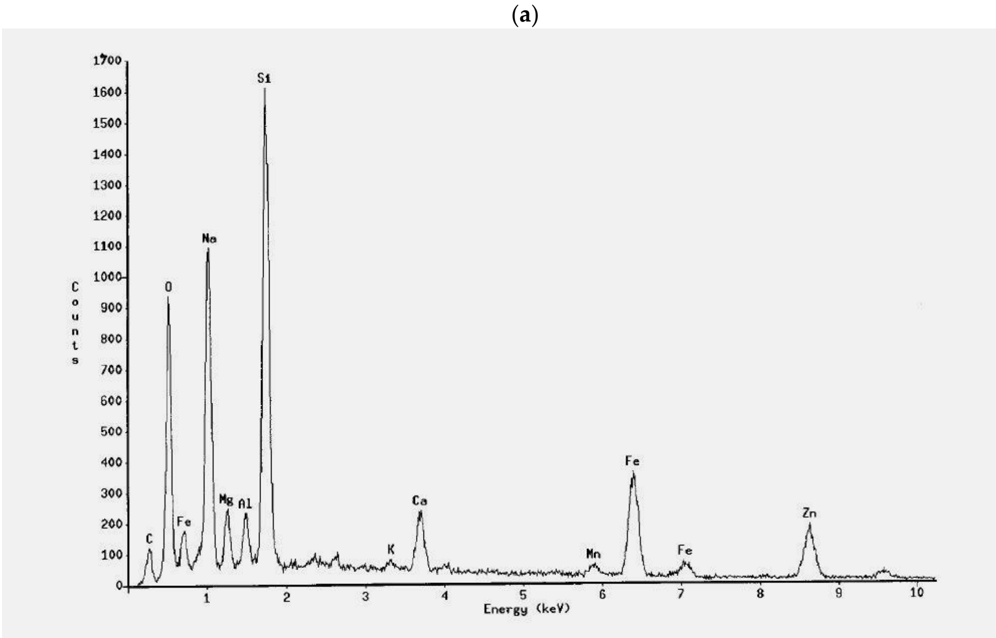
Figure 2. Results of SEM analysis of the dust before (**a**) and after (**b**) ISV treatment.

3.4. XAD Analysis Results of the Dust before and after ISV Treatment

Change in crystal structure could serve as a key indicator of successful vitrification. The dust was a crystalline substance that contained silicon, iron, and aluminum oxides. Vitreous substances, on the other hand, were amorphous substances. Therefore, X-ray diffraction was applied to examine the crystalline structure of the samples before and after vitrification. Figure 4 shows the results of XAD analysis of the dust before and after ISV treatment. According to Figure 4b, the SiO_2 crests disappeared in the processed dust, suggesting that the crystal structure was replaced with quasi-vitreous products after ISV treatment. Such a result corresponds to the studies of Ferraris et al. [21] and Kavouras et al. [10], which applied XRD and showed that solid waste became vitreous, amorphous substances after melting.



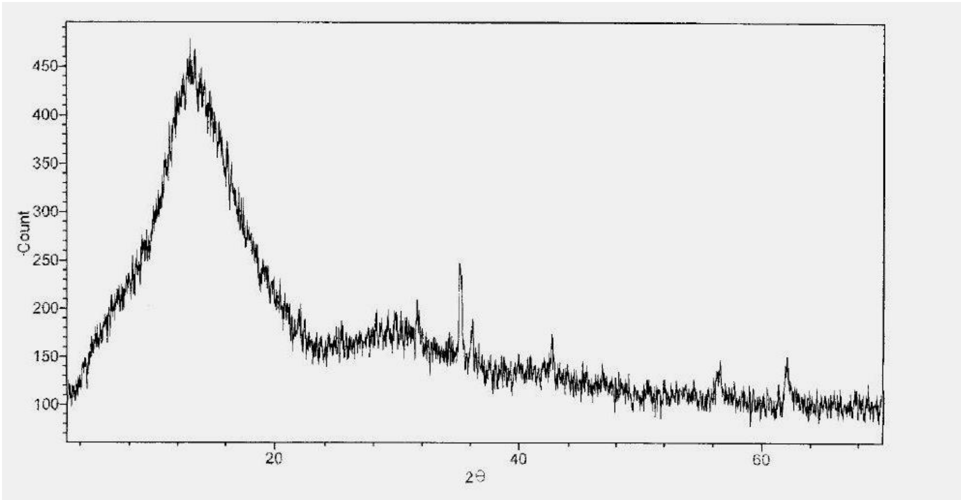
(**a**)



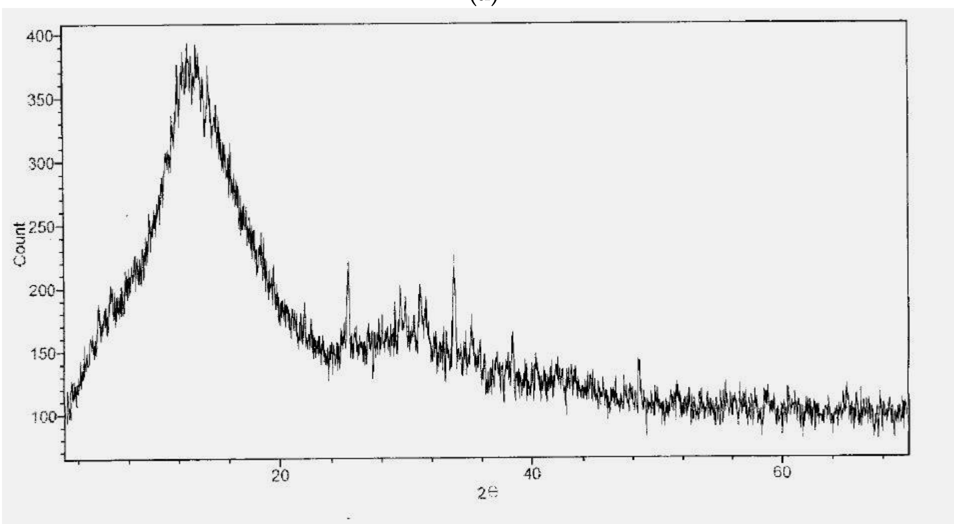
(**b**)

Figure 3. Results of EDS analysis of the dust before (**a**) and after (**b**) ISV treatment.

Baccaccini et al. [22] suggested that the crystal structure was replaced with vitreous products after ISV treatment but the crystal structure of the ISV products negatively impacted the durability of the products. Furthermore, it was also mentioned in the studies of Sheng et al. [23] and Rodrigo et al. [18] that the chemical durability of glasses was mainly determined by their composition. Therefore, the change in crystalline structure determined the weather resistance of the products after vitrification [9,12].



(a)



(b)

Figure 4. Results of XRD analysis of the dust before (a) and after (b) ISV treatment.

4. Conclusions

The subject of this study is the electric arc-furnace dust collected from an unidentified waste-disposal site in southern Taiwan. This study evaluates the stability of the final product after subjecting the dust to ISV treatment. First, the pH value of the dust reaches 11.68, indicating that the dust is a strong alkali. It is assumed that particles of the dust contain alkali substances. After the dust undergoes ISV treatment, it is gray in appearance with a crystal structure, while its hardness increases. Concentrations of heavy metals in the dust after undergoing ISV treatment fall below the limit stipulated by Taiwan's Environmental Protection Administration. This result indicates that although concentrations of heavy metals in the dust are relatively high, they can be degraded with effective time and temperature control during the ISV process. The findings of analyses of the dust before and after undergoing ISV treatment using an SEM and EDS, respectively, show that the surface of the final product after the dust undergoes ISV treatment is more compact than that of the dust before undergoing ISV treatment. There is a significant decrease in or elimination of wave-crest intensity of heavy metals in the dust after it undergoes ISV treatment. In other words, heavy metals in the dust are either encapsulated in or bonded to silicon lattices after the dust undergoes ISV treatment and are thereby barely leached from the dust. This study applied ISV technology to the remediation of an unidentified waste disposal site whereby pollutants are barely leached from the dust in question, while the final product is characterized by smaller size, high stability, excellent weather resistance, an innocuous nature, and recyclability. ISV technology can thus be practically applied to the remediation of unidentified-waste disposal sites. In addition, the technology can also be practically applied to the remediation of unidentified-waste treatment sites because it complies with increasingly strict environmental protection regulations.

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

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