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Geochemistry and soil chemistry reactions occurring during *in situ* vitrification

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Abstract

In situ vitrification (ISV) is a thermal treatment technology that permanently treats hazardous wastes. It was initially developed to treat soil contaminated with radioactive materials, and it is used to treat soils containing inorganic and organic chemicals. The ISV process introduces a substantial amount of energy into a relatively low-energy soil system. As a result, this energy increase affects naturally occurring processes and reactions which are governing the migration and degradation of chemicals in soil systems. This paper describes how ISV affects these naturally occurring processes and reactions. This paper concludes that although many mechanisms control chemical behavior, diffusion and convection are the main two factors that govern movement. Convection and concentration diffusion cause vaporized organic molecules to move toward the vitrified area and be destroyed or captured at the surface. Although thermal diffusion causes some molecules to move out to the transition zone up to 24 cm away, they will recondense and once again be drawn toward the vitreous zone by other mechanisms. The report also concludes that destruction mechanisms by pyrolysis and hydrolysis are also accelerated by the high temperature of the process.

Introduction

New and proposed U.S. environmental legislation has made landfill disposal very costly and will severely limit land disposal as an option for handling wastes. For example, the Superfund Amendments and Reauthorization Act (SARA) mandated that the U.S. Environmental Protection Agency (EPA) give priority to permanent, on-site, innovative treatment processes that reduce toxicity, mobility, and volume. In addition, Section 3004u of the Resource Conservation and Recovery Act (RCRA) gives EPA the authority to require a RCRA permit applicant to remediate inactive disposal units. Furthermore, the land ban requires that an increasing number of wastes be treated (a) prior to disposal, or (b) prior to redisposal of previously disposed wastes.

In addition to legislation, the extended liability associated with future environmental impairment of landfilling is making corporations consider treating waste within the plant or waste size boundary as the preferred option.

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The treatment of hazardous materials is becoming the preferred option in the United States and throughout the world. As a result, effective technologies to immobilize and/or destroy the materials either *in situ* for previously disposed wastes, or at the waste generation site, will play an increasingly important role.

In situ vitrification (ISV) is a thermal treatment technology that permanently treats hazardous wastes. It was originally developed to treat buried or disposed long lived (i.e. transuranic) radioactive wastes *in situ* and was first conceived in 1980, at Pacific Northwest Laboratories (PNL). A patent on the process is held by the U.S. Department of Energy (DOE), the sponsors of the initial research (U.S. Patent No. 4,376,598; 1983). After significant development effort and field scale demonstration, Battelle obtained license rights for non-radioactive applications to the ISV technology and created a new company, Geosafe Corporation, to commercialize the ISV process.

Initially, ISV was developed to treat soil contaminated with radioactive materials. It can treat soils containing organic constituents [1–3]. At the present time, ISV can be used to treat contaminated soil, process sludges, and tailings piles, and it is being tested and evaluated for treatment of (1) uncontrolled hazardous waste sites containing drums and (2) buried tanks that contain a hazardous heel in the form of either a sludge or slat cake.

The ISV process introduces a substantial amount of energy into a relatively low-energy soil system. As a result, this energy increase affects naturally occurring processes and reactions which are governing the migration and degradation of chemicals in soil systems.

This paper describes how ISV affects these naturally occurring processes and reactions. First, this paper generally describes the ISV process. Then, this paper discusses the pertinent geochemical and soil chemistry processes and reactions that ISV affects.

General description of the ISV process

In situ vitrification is a thermal treatment process that transforms contaminated soil into silicate glass and a crystalline product, similar, if not identical, to obsidian. The principle of ISV operation is based on joule heating: electrical current is transformed into heat, which increases in magnitude as the current continues to pass through the molten mass. This is the same process the glass industry utilizes to produce every day glass products, only the glass industry furnaces operate at much lower temperatures because additives are employed to reduce the melting point, change color, enhance clearness, etc.

Figure 1 depicts the ISV process and Fig. 2 is a schematic diagram of the ISV equipment system. Electrical current is delivered to subsoil by electrodes. A square array of four molybdenum/graphite electrodes is inserted into subsoil to the desired treatment depth. Each electrode is comprised of a 5-cm-diameter

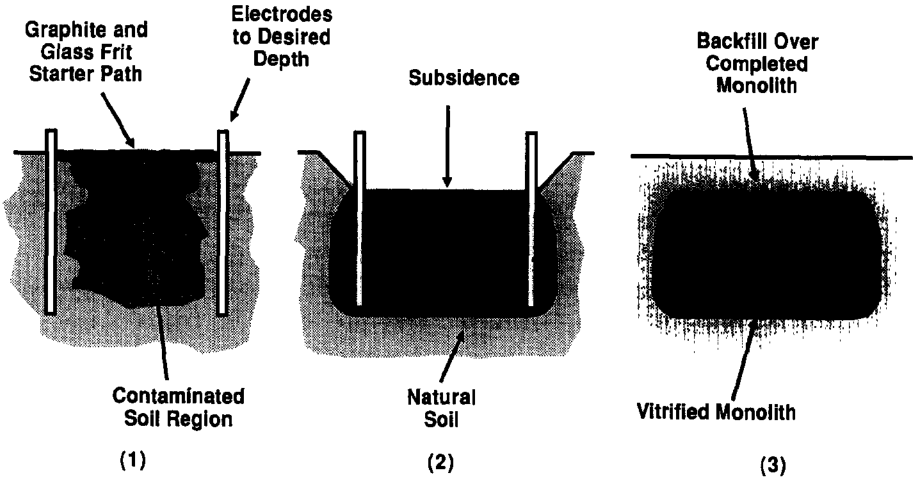

Fig. 1. Stages of ISV processing.

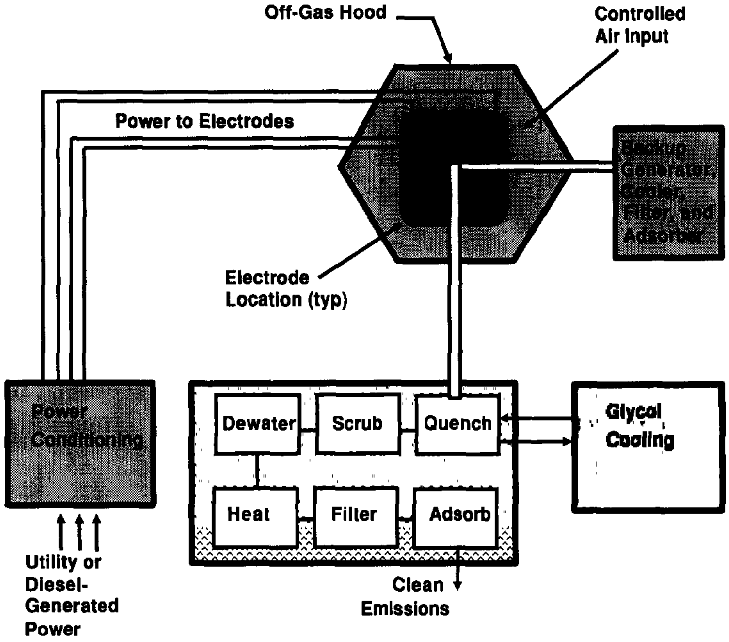

Fig. 2. *In situ* vitrification equipment system.

molybdenum core inside a 30-cm-diameter graphite collar [4]. This electrode design was developed to promote cold-cap subsidence and to obtain reliable electrode performance during an entire single setting (up to 400 h). Cold cap subsidence refers to the suppression of the porous glass layer that tends to form on the surface of the melt.

The graphite collar provides a relatively inexpensive, large diameter (30 cm) cross-section that promotes conduction of heat to the surface of the melt. The molten surface aids the release of gases – primarily water and carbondioxide – generated during the process [4]. The graphite collar also promotes gas release because molten soil does not wet graphite as it does molybdenum; it provides a mechanism for gas release between the graphite/melt interface [5].

Because unmelted soil is not sufficiently conductive to initiate the process by itself, a conductive mixture of flaked graphite and glass frit is placed between the pairs of electrodes as a starter path. An electrical potential is applied to the electrodes to establish an electric current in the starter path. The electrical potential heats the starter path and surrounding soil to 2,000 °C, well above the initial soil-melting temperature of 1,100 to 1,400 °C. The graphite starter path is eventually consumed by oxidation, and the current is transferred to the electrically conductive molten soil (i.e. melt).

The ISV technique seeks its own equilibrium melting temperature, depending on the fusion temperature of the soil and the particle sizes encountered. In general, ISV creates a melt that can attain temperatures greater than 1,700 °C (3,092 °F) [6].

When a higher fusion temperature layer or a large particle size (greater than 2 cm) layer is encountered, a higher equilibrium temperature is needed to achieve the same downward progression rate for the melt. Engineering approaches such as injecting fluxants (e.g., soda ash, lime, and glass frit) into the voids of rock layers can be used to enhance the downward melting rate, if necessary [5].

The melt grows at a rate of about 3 to 6 cm/h (or one to two inches/h). The shape of the melt is roughly a cube with slightly rounded corners (see Fig. 1), a shape that reflects the higher power density around the electrodes. As the melt grows in size, the resistance of the melt decreases, making it necessary to periodically adjust the ratio between the voltage and the current to maintain operation at constant power, according to the power equation:

$$P=I^2\times R \tag{1}$$

where P is power, I is current, and R is electrical resistance. This is done by adjusting the tap positions on the power supply to the electrodes on a secondary side of the transformer equipped with multiple voltage taps and a saturable reactor power controller. The multiple taps allow for more efficient use of the power system by maintaining the power factor (the relationship between current and voltage) near maximum. Fourteen effective taps permit adjusting the voltage from a maximum of 4000 V to a minimum of 400 V per phase and the current from 450 A to 4000 A per phase. As the melt grows downward and outward, power is maintained at sufficient levels to overcome the heat losses from the surface and to the surrounding soil.

Melt depth is limited as the heat losses from the melt approach the energy level that is deliverable to the molten soil by the electrodes [4]. Generally, the melt grows outward to about 50% of the spacing of the electrodes. If the electrode spacing is 5.4 m (18 ft), a melt width of about 8.5 m (28 ft) would be observed under nominal conditions. Full-scale ISV units are designed to operate to depths of 4.57–6.10 m (15–20 ft).

The effluents exhausted from the hood, primarily water vapor and air, are cooled and treated in the off-gas treatment system. In general, the system cools, scrubs, sorbs, and filters the effluents exhausted from the hood in three stages [7]. First, gases are cooled in a quencher and scrubbed in a tandem nozzle scrubber to remove particles. Second, most of the water in the saturated gas stream is removed by a vane separator, a condenser, and a second vane separator. Third, the off-gas is heated to a point where it becomes unsaturated. The gas is then filtered through two high efficiency particulate air filters and exhausted by an induced blower fan [6].

General description of the full scale process equipment

Figure 3 is a drawing of the deployment of field equipment for full scale operation. The process equipment required to perform these functions includes (1) electrical power system, (2) off-gas hood, (3) off-gas treatment system. Details of the process equipment are found in Buelt and Carter [8] and FitzPatrick et al. [9].

Except for the off-gas hood, all components are contained in three transportable trailers: an off-gas and process control trailer, a support trailer, and an electrical trailer. These trailers are mounted on wheels to facilitate travelling to any site over a compacted ground surface.

The off-gas hood and off-gas line, which are installed on the site for collection of the gaseous effluents, are dismantled and placed on a flatbed trailer for transport between the sites to be treated.

The primary components in the off-gas treatment system trailer include a

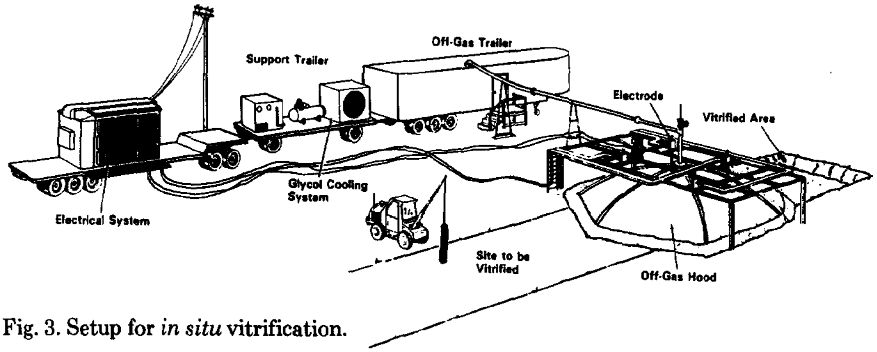

Fig. 3. Setup for *in situ* vitrification.

gas cooler, a wet scrubber system (tandem nozzle scrubber and quencher), a heat exchanger, process scrub tank, scrub solution pump, a condenser, two mist eliminators (vane separators), a heater, a filter assembly, and a blower system. The support trailer contains the glycol cooling system. This system interfaces with the scrub solution and extracts the thermal energy that builds up in the off-gas treatment system from cooling the combustion gases from the hood. The head is transferred to the atmosphere in a fin tube, air-cooled heat exchanger. The entire process system is therefore self-sufficient in terms of site services, except for the electrical supply.

For routine operations on a site, the three trailers are coupled together and moved from one processing position to another.

ISV Processing rate, time, and costs

The normal processing rate for the large-scale system is 4 to 5 metric tons/hour, a rate competitive with many other remediation technologies. The average processing operation requires approximately 150 to 200 h, depending on the depth and electrode spacing. Moving from one processing position to another requires approximately 16 h. This period also provides time for performing routine equipment maintenance.

The cost for ISV processing is highly variable and site-specific; it depends upon (a) amount of site preparation required, (b) soil/waste properties, (c) volume to be processed, (d) depth of processing, (e) soil/waste moisture content, (f) unit price of electricity, and (g) season of the year. Processing costs range nominally from \$300–\$350/ton [10].

Wastes and chemicals treated via ISV

Pacific Northwest Laboratory began developing ISV technology in 1980 under contract to the DOE. The first large-scale test of ISV at an actual contaminated soil site was performed at the 216-Z-12 Crib on the Hanford Site near Richland, Washington. The Z-12 site contains primarily transuranic materials that have been previously disposed [4,5,8].

Since 1980, 90 separate experimental tests with a variety of conditions and waste types have been conducted. These include 20 pilot-scale tests processing 10–50 metric tons of contaminated soil during each test, and 6 large-scale tests processing 400–800 tons during each test.

Table 1 lists the different waste materials that have been treated by ISV. At least 13 metals, nine radioactive elements, 10 liquid organics, and 11 solid organic wastes have been successfully treated. The mechanisms by which ISV treats metals and other inorganic chemicals are different from mechanisms by which it treats organic chemicals. Inorganics which are not volatilized are treated by incorporation into the three-dimensional structure of the obsidian-like glass that forms when the melt cools. This mechanism is discussed in the following section on geochemistry. Organics are treated by (a) pyrolysis in the

TABLE 1

Chemicals and wastes processed by ISV

Aldrin
Aluminum
Americium
Anthracene
Arsenic

Barium
Benzene
Bis(2-ethylhexyl)phthalate
Bismuth
Buna rubber

Cadmium
Carbon tetrachloride
Cesium
Chlordane
Chromium
Cobalt
Copper
Cotton

DDD
DDE
DDT
Dichlorobenzene
Dieldrin
Dioxin

Ethylene glycol

Ferric nitrate
Fluoranthene

Hydrofluoric acid
Hydroquinone

Ion exchange resin
Iron

Lead

Mercury
Methylene chloride
Methyl ethyl ketone

Neoprene
Nickel
Nitric acid

Paper
PCBs
Phenanthrene
Plutonium
Polyethylene
Polypropylene
Potassium hydroxide
Potassium sulfite
PVC
Pyrene

Radium 226

Radon 222
Ruthenium

Sodium formaldehyde bisulfate
Sodium hydroxide
Sodium nitrate
Sodium sulfite
Stoddard solvent
Strontium
Sulfuric acid

Technetium
Thorium
Teflon
Toluene
Trichloroethylene

Uranium

Wood

Zinc
Zirconium oxide

melt, in the pyrolysis zone, and in the off-gas hood upon mixing with heated air, (b) accelerated chemical reactions in soil surrounding the melt and the pyrolysis zone, and (c) removal from soil and physical treatment in the off-gas system. The mechanisms involving the transport and *in situ* treatment of organics are discussed in the section on soil chemistry.

Geochemistry reactions

The previous section (Description of the ISV process) revealed that heat generated by the applied electrical current melts soil and creates a melt that can attain temperatures greater than 1,700°C (3,092°F) [6]. Radionuclides, nonvolatile hazardous elements, and metals are incorporated into the melt as it grows.

The ISV mechanism of melt production and solidification is similar to the natural geochemical reactions that create igneous rocks on earth. This section will discuss these natural reactions and relate them to the melt production and solidification by ISV.

Geochemical reactions forming igneous rocks

Molten rock, known as magma, exists beneath the earth's crust. Magma is a melt, a complex liquid solution at high temperature that contains solid and gaseous materials. As this melt loses heat and its temperature falls, the melt solidifies to form igneous rock [11].

The melt can solidify to form igneous rock via two pathways. The first involves slow cooling; the second, rapid cooling.

During the first pathway, the melt may remain trapped within the crust, slowly cool, and solidify to form a crystalline igneous rock. Ninety-five percent of the outermost 10 km of the earth's crust is composed of rocks of igneous origin [11]. The melt solidifies into rock through the process of crystallization. The rate at which the melt cools influences the chemistry and texture of the resulting rock. For example, when a melt cools slowly deep within the earth's crust, a high degree of fractionation (i.e. separation of crystals and liquid) can occur, resulting in a rock with different chemistry than the original melt and with large, well developed crystals.

During the first pathway, the time required for crystallization of a large mass of magma varies from 700 years for a 200 meter thick sill to 10 million years for a large granitic batholith [12].

Formation and stability of naturally occurring obsidian through geochemical reactions

During the second pathway, if a melt is suddenly ejected from a volcano or a fissure at the earth's surface, it may cool rapidly; as a result, there is insufficient time to allow nucleation sites to form and crystals to form. However, the melt does cool and forms glass rock, or what is commonly known as obsidian (silicate glass). Almost any rapidly cooling melt at the earth's surface can form a glass. Glass is a special type of solid in which the ions are not arranged in an orderly three-dimensional structure. As a result, the fracture mechanism is conchoidal. The rock also resists weathering by freeze/thaw mechanisms that accelerate natural degradation.

Probably the most commonly known, naturally occurring glass is obsidian, which is also known as glassy granite. It is dense and black, but somewhat translucent on its edges.

The long-term stability of obsidian at the earth's crust is controlled by three mechanisms: alteration (weathering), devitrification (recrystallization), and hydration (water absorption) [13,14]. The weathering process of obsidian in a natural environment that is not saturated with free water involves the hydration of atmospheric water that is absorbed on the rock surface. The water then diffuses into the obsidian as a function of time and temperature. Based on studies of the mean age of natural glass rock, obsidian has a mean life of about 18 million years [13].

Formation and stability of ISV-derived obsidian

The ISV mechanism of melt production and solidification is similar to the natural reactions that create igneous rocks on earth. A typical soil is primarily composed of silica and aluminum oxides which have melting temperatures between 1,100 to 1,600°C (2,012–2,912°F) [6]. During ISV, heat generated by applying electrical current to soil creates a melt that can attain temperatures greater than 1,700°C (i.e. 3,092°F) [6].

When this melt cools, it forms a glass rock with a relatively uniform chemical composition. The melt is not a static volume of molten soil: it experiences convective flow. Convective flow causes a continual mixing of the melt that creates a uniform chemical distribution and composition within it.

When this melt cools, it forms a glass with a random atomic structure, composition, and weathering characteristics that is basically the same as obsidian [15]. Because the ISV-derived obsidian is a glass with a random atomic structure, its fracture mechanism is conchoidal and has no preferential planes of weakness. Tests on ISV-derived obsidian show that its durability is similar to that of granite [6].

The durability of ISV-derived obsidian can be estimated by examining the durability of obsidian. The previous subsection stated that the weathering process of obsidian in a natural environment that is not saturated with free water involves the hydration of atmospheric water that is chemically adsorbed on the surface. The water then diffuses into the obsidian as a function of time and temperature. This weathering process would be expected for the ISV-derived obsidian because of its chemical and physical similarity to obsidian [4].

In the natural environment, obsidian has a hydration rate constant of 0.0016 to 0.03 mil^2 (1 to 20 μm^2) per 1,000 years (Larsen and Langford, 1978). Using a linear hydration rate of 0.016 mil^2/1,000 y (10 μm^2), FitzPatrick et al. [2] derived a highly conservative estimate of a $\ll$40 mil (1 mm) hydrated depth for the ISV-derived obsidian over a 10,000-year time span. In other words, the ISV-derived obsidian should maintain its structural integrity for at least 10,000 years. In reality, the removal of Na^+, Ca^{2+}, K^+ and Mg^{2+} ions and subsequent formation of a surface rind of Al, Si, Fe and OH ions during hydration inhibits further hydration, thus slowing the hydration reaction.

The release of Na^+ is a measure of the extent of hydration of a glass; in addition, its normalized release divided by the density of the glass is the depth of hydration [15]. Buelt et al. [4] reported data for the release of Na^+ from ISV-derived obsidian from Hanford soil during a leach test at 90°C for 7, 14, and 28 days. Using these data, the hydration rate at 194°F (90°C) appears to be about 0.0032 mil^2 (2 μm^2/y). In the literature on field studies of obsidian hydration, the hydration rate obeys an Arrhenius relation with an activation energy of 20 kcal/mol [14]. Applying this to the hydration of ISV-derived obsidian, a rate of 0.008 mil^2 ($5\,\mu\mathrm{m}^2$)/1000 y at 77 °F (25 °C) was predicted for glass exposed to air [15]. A rate of 0.0016 mil^2 ($1\,\mu\mathrm{m}^2$)/1000 y at 50 °F (10 °C) was predicted for glass buried below grade [15] These values are comparable to those found for obsidian hydration rates in the field for similar average weathering temperatures.

Considering the similarity of the ISV-derived obsidian to naturally occurring obsidian, the mean life of the ISV-derived obsidian would be on the order of 1 million years.

Leaching of inorganic chemicals from ISV-derived obsidian

The total concentration of any chemical, C_{total}, in a soil or a geologic material is equal to:

$$C_{\text{Total}} = C_{\text{Fixed}} + C_{\text{Adsorbed}} + C_{\text{Water}}, \tag{2}$$

where C_{Fixed} is the concentration of fixed chemical comprising part of the structure of clay and soil minerals, in mg chemical/kg soil, C_{Adsorbed} is the concentration of chemical adsorbed onto the surface of soil minerals and onto organic matter exchange sites in mg chemical/kg soil, and C_{Water} is the concentration of chemical in soil water or groundwater in equilibrium with C_{Adsorbed}, in mg soluble chemical/kg soil. The "immobile" fraction of C_{Total} is represented by C_{Fixed}. The sum of C_{Adsorbed} and C_{Water} represents the potentially mobile portion of C_{Total} [16].

In soil prior to treatment with ISV, the relative magnitudes of the parameters listed in eqn. (2) generally are:

$$C_{\text{Fixed}} > C_{\text{Adsorbed}} > C_{\text{Water}}$$

The greater part of C_{Total} exists as C_{Fixed} and is immobile. Because treatment with ISV incorporates radionuclides, nonvolatile hazardous elements, and metals into the melt which then solidifies as an obsidian-like glass with a random three-dimensional chemical structure, C_{Total} should be transformed into immobile C_{Fixed}. If this is the case, then results of leaching tests should show relatively minor amounts of leachable inorganics.

Obsidian ((ISV-derived) has been subjected to a variety of leach tests, including the EPA's Extraction Procedure Toxicity Test (EP Tox) and Toxic Characteristics Leach Test (TCLP). All of these tests show a uniformly low leach rate for heavy metals of about 5×10^{-5} g/cm^2·day or lower [4]. Leaching studies of ISV-treated Hanford soil were conducted to determine its chemical durability. Two types of leach tests were performed on ISV-field test products: a 24-h soxhlet test in 99 °C deionized water and a 28-day Materials Characterization Center Test (MCC-1) in 90 °C solutions of deionized water, silicate

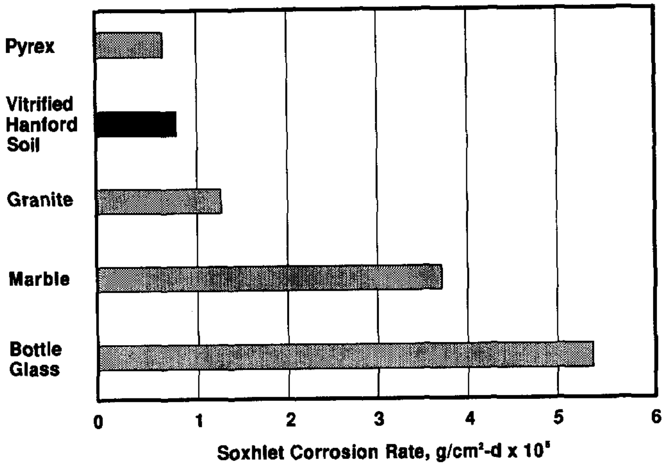

Fig. 4. Leach resistances of selected materials.

water, and brine. A comparison of the resulting corrosion rate during soxhlet leaching with published data [17,18] is provided in Fig. 4; an analysis of these data show that the bulk leach rate of ISV-derived obsidian is significantly less than that of marble or bottle glass and is comparable to Pyrex and granite [4,19].

Soil chemistry processes and reactions during ISV

Several soil chemistry reactions and processes govern the migration and degradation of chemicals in soil. The presence of a mélt in subsoil has a substantial effect on these. This section will discuss those reactions and processes affected by the ISV processing of soil.

Accelerated chemical reactions

Figure 5 illustrates a melt and its immediate environment. The high temperature of the melt zone and the pyrolysis zone destroys organic chemicals via pyrolysis [7]. Pyrolysis is the thermal decomposition of an organic chemical in the absence of oxygen. As the melt zone grows in volume, the melt and pyrolysis zones pyrolize organic chemicals present in soil they engulf.

The pyrolyzed byproducts can migrate through the melt, to the surface of the melt, and burn in the presence of oxygen. In addition, the pyrolyzed byproducts can migrate next to the electrodes which act as gas release vents, allowing preferential flow of contaminants through the melt; like water on wax, molten glass does not wet the surface of graphite, thereby creating a path to the hood.

Immediately adjacent to the pyrolysis zone is a heat affected or dry zone about six to nine inches in width. The dry zone is a path of low resistance to organic chemical migration as a gas. At this location, the soil possesses a higher air-filled pore space relative to the ambient zone soil due to a lack of water. The lower boundary of the dry zone is a 100 °C isotherm.

Adjacent to the dry zone is the transition zone. This zone is about nine inches in width. As the molten glass boundary moves down through the soil during ISV processing, the soil ahead of the advancing molten glass is heated to 100 °C as water is vaporized.

Adjacent to the transition zone is the ambient zone which contains soil at ambient conditions. This zone displays the highest resistance to gas and vapor migration due to higher water saturations.

In general, several organic chemical reactions are known to occur in soil systems: hydrolysis, substitution, elimination, oxidation, reduction, and surface-catalyzed hydrolysis and oxidation [16,20–24]. ISV processing of soil can affect chemical reactions primarily in two different ways.

First, chemical reactions occur at accelerated reaction rates in soil during ISV processing due to increased soil temperature. The rate of reaction of any organic chemical reaction, k, can be expressed as:

$$k = CF \times EF \times OF, \tag{3}$$

where CF denotes the collision frequency, EF the energy factor, which is inversely proportional to the activation energy of a reaction, E_a ($EF \sim 1/E_a$), and OF the orientation factor.

The number of collisions among molecules of chemicals present in the soil system, CF, will increase as soil temperature increases; as a result, the chemical reaction rate, k, accelerates as soil temperature increases.

Second, hydrolysis reactions will occur at an accelerated rate for many organic chemicals whose reaction rates are dependent upon soil acidity. The pH at soil particle surfaces in acid soils can be as much as 4 pH units lower than the pH of the water phase of a soil system, due to the greater accumulation of H^+ at soil particle surfaces relative to the water phase. For example, the strength of acid sites on a dried kaolinite was measured and found to be comparable to 90% sulfuric acid [24]. As a result, an organic chemical susceptible to acid-catalyzed hydrolysis can have a shorter half-life at or near particle surfaces than in the water phase of a soil system.

The water content of soil can affect the hydrolysis rate of organic chemicals, based on the research involving a few chemicals. For example, the addition of water to kaolinites to the limits of adsorbed water, approximately 11%, resulted in 95% degradation of methyl parathion and parathion in five days [23]. An increase in soil moisture content above 11% resulted in a steep decrease in the degradation rate to between 10 and 50% in 15 days. The mechanism, at low soil moisture content, presumably involves the presence of more organic molecules in the region near the soil surface where pH is lower.

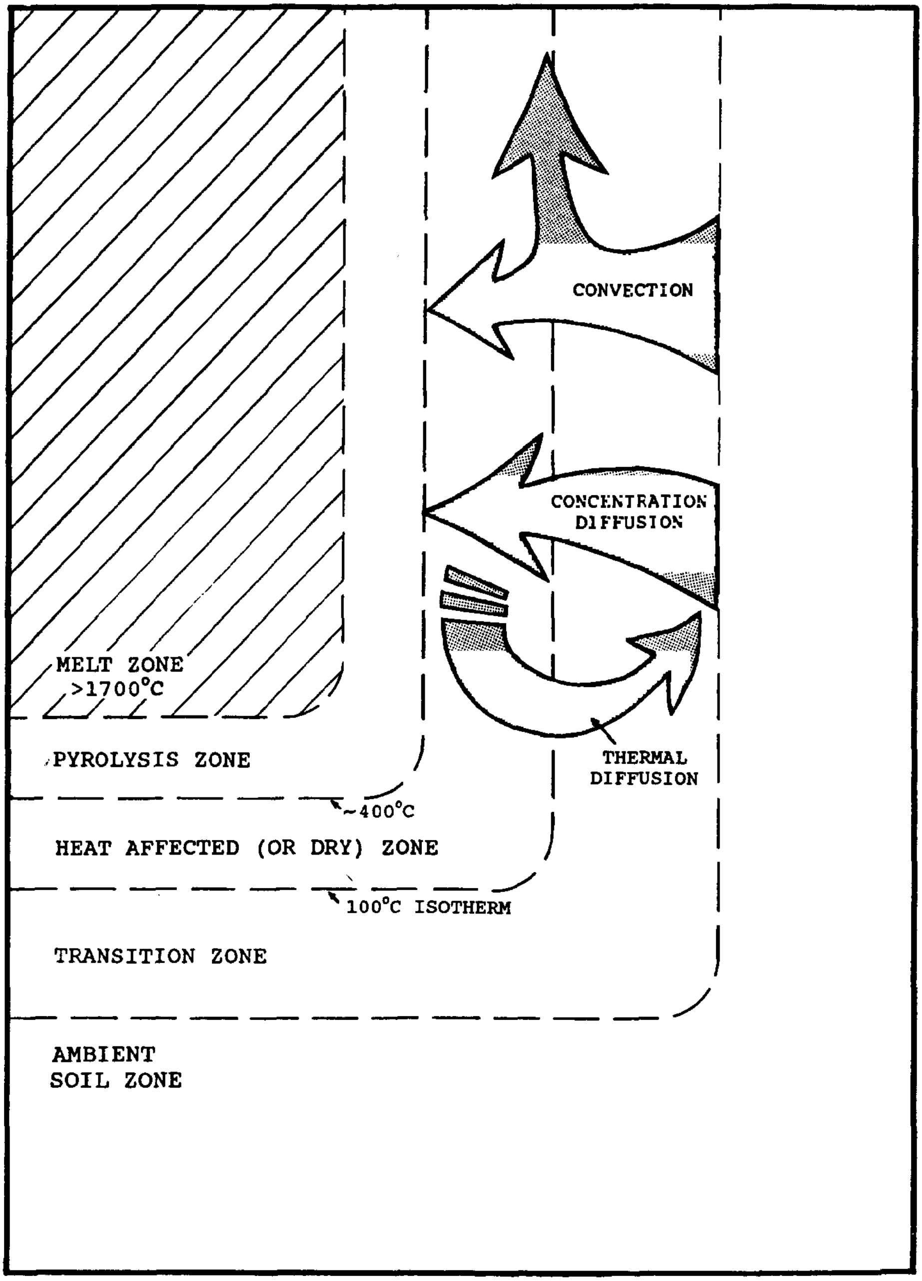

Fig. 5. Chemical reactions and processes occurring within and near the melt.

Because ISV processing decreases the soil water content in the transition zone and the dry zone, greater acidity near the soil particle surfaces should occur and cause an increase in organic chemical hydrolysis rates. However, for most organic chemicals, the rate of advance of the melt probably will make pyrolysis the primary pathway of degradation.

Concentration diffusion

Some chemicals can migrate via diffusion through soil air. Diffusion is defined as the average rate of migration or velocity of a chemical in soil air [16]. Diffusion of an organic chemical can be driven by three different gradients: concentration, temperature, and pressure. Generally under typical soil conditions, only concentration diffusion is important [16].

Diffusion which is primarily dependent upon a concentration gradient is known as concentration diffusion or ordinary diffusion. The most commonly utilized relationship describing concentration diffusion is Fick's first Law:

$$\mathrm{d}q/\mathrm{d}t = -D_A(\mathrm{d}c/\mathrm{d}x), \qquad (4)$$

where $\mathrm{d}q/\mathrm{d}t$ is the rate that a chemical moves past a given point per unit cross-sectional area (flux), c is the concentration of the chemical, x the distance, D_A the diffusion coefficient in air, and $\mathrm{d}c/\mathrm{d}x$ the chemical's concentration gradient in the x-direction and perpendicular to the cross-sectional area.

Since D_A is always positive, the negative sign in eqn. (4) indicates that diffusion occurs in the opposite direction from the concentration gradient, i.e., from higher to lower concentrations. An analysis of eqn. (4) shows that during concentration diffusion, chemicals migrate from regions of higher concentration to regions of lower concentration; the greater the concentration difference, the greater the diffusion rate.

The high temperature in the melt and pyrolysis zones pyrolizes organic chemicals present in soil as these zones grow in volume en engulf soil. As a result, the melt and pyrolysis zones create a concentration diffusion gradient toward themselves.

It is most important to recognize that when any chemical reaches its vapor point temperature (i.e. its boiling point), it becomes a vapor and then obeys the laws of gases. The pyrolysis and melt zones' high temperatures (i.e. greater than 1,700 °C or 3,092 °F) exceed the vapor point (and destruction temperature) of almost all organic chemicals. Therefore, as the melt and pyrolysis zones grow and engulf soil, they vaporize organic chemicals that, under normal soil conditions, would not migrate.

These vaporized organic chemicals will increase in temperature as they approach the melt and pyrolysis zone to the point that they undergo pyrolysis. The chemical's concentration at that point is diminished; as a result, a concentration gradient towards the melt and pyrolysis zone results in continued mass transfer of the organic chemical by diffusion toward the zones.

Thermal diffusion

An analysis of Fig. 5 shows that a thermal gradient of at least 1,700 °C or 3,092 °F exists between the melt and the ambient soil zone, over a relatively short distance of less than two feet. Thermal gradients cause diffusion; diffusion which is primarily dependent upon a thermal gradient is known as thermal diffusion.

Thermal diffusion will cause some molecules of the organic chemical to migrate away from the melt and pyrolysis zones (see Fig. 5) in an attempt to establish an equilibrium that compensates for the effects of concentration diffusion. However, vapors cannot move to cooler locations beyond the vapor point isotherm without recondensing. As a result, the ambient soil zone remains a barrier where ambient conditions control chemical migration.

At the point of recondensation, concentration diffusion resumes control of chemical movement (as illustrated in Fig. 5). Migration toward the melt and pyrolysis zones resumes, and pyrolysis continues to lower the concentration of the organic chemical. As a result, concentration enrichment does not occur at locations cooler than the vapor-point isotherm and in the ambient soil zone.

It is important to recognize that the concentration and thermal diffusion occur extremely rapidly in the dry zone and transition zone. The rates of concentration and thermal diffusion of organic chemicals are greater in the dry zone and the transition zone than in the ambient soil zone. The general overall effect of increasing temperature is an increase in the chemical's diffusion rate [25]. In general, the following equation [26], which was derived for hexachlorobenzene, can be used to obtain a gross estimate of how temperature affects the diffusion coefficient, D_A, of an organic chemical:

$$D_{A2} = D_{A1}(T_1/T_2)^{1/2}, \qquad (5)$$

where D_{A1}, D_{A2} are diffusion coefficients, and T_1, T_2 temperatures (K).

Using eqn. (5) and assuming that the relationship holds for large temperature differences, a 1,700 °C temperature difference causes a 6.7× increase in the diffusion coefficient; in other words, diffusion would occur 6.7× faster near the melt than in the ambient soil zone.

Pressure diffusion

Diffusion caused by a total pressure gradient is known as pressure diffusion. However, pressure diffusion is only significant during processes utilizing extreme pressure gradients (e.g., centrifugation). For average soil conditions, pressure gradients are not expected to be significant during ISV.

Gaseous convection

The migration of organic chemicals near the melt can be significantly affected by gaseous convection, which is also known as carrier-gas transport.

Gaseous convection results when an organic chemical is swept along the flowpath of another gas present in much higher quantities.

During ISV processing of soil, the amount of gas generated from the decomposition of humus and other natural chemicals within the soil is insignificant. Some gas generation can occur when an advancing melt penetrates a drum containing combustible materials or when the advancing melt intrudes soil inclusions that contain combustible solid or liquid materials.

Water vapor is the predominant gas present within the treatment zone that acts as a carrier gas during ISV processing. Water is usually present in soil in the 5 to 30 wt.% (percent by weight) range, whereas hazardous contaminants are usually present at concentrations well under 1 wt.%.

Movement of water vapor and organic chemical vapors within the dry zone is dependent upon the void volume of the soil. In other words, the soil moisture content affects the soil diffusion constant, D_{SA}, for a chemical. At higher soil moisture contents, the cross-sectional area where diffusion can occur will be relatively smaller. As a result, D_{SA} is smaller in magnitude. Likewise, as soil moisture content decreases due to a soil temperature rise from an advancing melt, D_{SA} must also increase. A modified version of Fick's first law for diffusion [16] mathematically describes these two factors:

$$\text{Flux} = -D_{SA}(dc/dx) = -A(P_{SA} - P_B)D_A(dc/dx), \tag{6}$$

and

$$-D_{SA} = -A(P_{SA} - P_B)D_A, \tag{7}$$

where D_A is the diffusion coefficient in unobstructed air, D_{SA} the diffusion coefficient in soil air, A a correction factor for soil tortuosity, P_{SA} the soil porisity (the fraction of open volume in soil), and P_B the volume of blocked pores.

The maximum void volume resides in the dry zone because water is absent. Vapor migration within the dry zone is assisted by the negative pressure (0.5 to 1.0 inches of water) existing under the off-gas collection hood.

It is most important to recognize that water is a chemical; therefore, data and information on water and water vapor movement in soil will give us valuable information and insight into how other chemicals behave in soil. Repeated ISV tests have demonstrated that water vapor moves upward to the soil surface where it is captured in the hood and treated by the off-gas treatment system.

Material balance measurements during ISV field tests have confirmed this behavior. A water mass balance was performed to demonstrate that the soil moisture is completely removed by the ISV process [5]. The water mass balances are achieved by the following:

$$m\, X_{H_2O}/P + V_{air}\, Yi_{H_2O}\, d/P = V_{air}\, Ye_{H_2O}\, d/P + V_{liq}, \tag{8}$$

where m is the mass of soil dried during the large-scale test (kg), X_{H_2O} the mass fraction of water in the soil, P the density of water, V_{air} the volume of air drawn through the hood during the test, $Yi_{\mathrm{H_2O}}$ the volume fraction of water vapor in ambient air, d the density of water vapor, $Ye_{\mathrm{H_2O}}$ the volume fraction of water vapor in the stack, and V_{liq} the accumulation (or loss) of scrub liquid in the tanks.

During the test, a 700 ton mass of soil was vitrified; the weight of this soil plus the weight of 23 cm of dry soil surrounding the vitrified block is about 750 tons. With a 4.5 wt.% soil water content, approximately 33,800 L of water were removed during the test. With ambient conditions varying from 28°C at 25 wt.% humidity to 15°C at 71 wt.% humidity during the test, the equivalent amount of water drawn into the hood from outside air was 9000 L. The amount of water lost from the scrub tanks, V_{liq}, was −5100 L. Because a humidity meter was not located on the stack, $Ye_{\mathrm{H_2O}}$ was based on 100% saturation at the exit of the scrub system's mist eliminator. The average temperature at this point was 30°C. At 30°C, the equivalent amount of water exhausted from the stack was 47,500 L.

Using these parameters and solving eqn. (8), the left and right sides of the mass balance equation are equivalent (42,800 L versus 42,400 L). Therefore, water associated with the soil being treated is completely removed by the process before being released to the atmosphere.

In addition to water balance measurements, the findings from radio frequency *in situ* soil decontamination [27] also support the conclusion that water vapor moves upward to the soil surface where it is captured in the hood and treated by the off-gas treatment system. Migration of chemicals into and out of the heated zone was assessed by injecting a tracer into the soil and by sampling soil in zones immediately outside the perimeter of the heated volume. Halon was injected four feet (1.2 m) outside the heated volume at a depth of six feet (1.8 m) and was detected approximately 107 minutes later in the raw gases being collected from the heated zone; this shows that soil gases and liquids were moving into the heated zone from adjacent soil outside of the heated zone. In addition, there was no net migration of chemicals from the heated area to the surrounding soil.

Capillary water migration

Liquids present in soil will move from locations of thicker to thinner films, and toward regions of lower film (surface) tension [16]. Because the melt is surrounded by a dry zone, capillary water and chemicals present in capillary water are drawn to the dry zone and towards the melt. Capillary water moves in this direction until such time that it is vaporized. Chemicals present in capillary water move in this direction towards the melt until the vapor-point isotherm is encountered, at which time the chemical becomes a part of the vapor phase.

The rate of capillary movement is very slow, on the order of days or longer to migrate a few inches [28–30]. However, the melt advances at a rate of about 3 to 6 cm/h. Therefore, the melt advances at a rate that overtakes the ability of capillary forces to move significant amounts of water, and chemicals dissolved in water, to the melt.

Adsorption of water and chemicals onto soil particle surfaces

Adsorption is defined as the accumulation of a chemical at the surface of soil particles with a decrease in the concentration of the dissolved chemical in water [16].

In the ambient zone, adsorption is the primary process which significantly retards the movement of many organic chemicals. The importance of this process can be illustrated by estimating the diffusion time for a PCB molecule to travel six inches. This approximation can be obtained by using eqs. (9) and (10) [31]:

$$t_D = l^2/D_E, \tag{9}$$

where t_D is the diffusion time (days), l the distance traversed by the chemical, and D_E the effective soil diffusion coefficient (m^2/day),
and D_E is given by:

$$D_E = [(D_A K_H P_{sa}^{10/3}/P_T^2) + (D_W (WC)^{10/3}/P_T^2)] \times (P_b K_d + WC + P_{sa} K_H)^{-1}, \tag{10}$$

where D_A is the diffusion coefficient of the chemical in air (m^2/day), K_H is Henry's Law constant (dimensionless), P_{sa} is the soil air content (m^3/m^3), P_T the soil total porosity, D_W the diffusion coefficient of the chemical, in water (m^2/day), WC the soil water content (m^3/m^3), P_b the soil bulk density (kg/m^3), and K_d is the adsorption or distribution coefficient (m^3/kg).

To solve these equations, the following values for D_A, K_H, P_{sa}, P_T, D_W, WC, P_b, and K_d will be utilized:

D_A = 0.372 m^2/day (estimated by utilizing eqn. 7.4 and the diffusion coefficient for chlorotoluene obtained from Table 7.1, both from Dragun [16]),
K_H = 0.0332 (derived using $P_V = 0.0000771$ mmHg and $S = 41$ μg/liter),
P_{sa} = 0.30 (a typical value for the soil air content),
P_T = 0.40 (a typical value for soil total porosity),
D_w = 5×10^{-6} cm^2/s (4×10^{-5} m^2/day),
WC = 0.1 (difference between P_T and P_{sa}),
P_b = 1350 kg/m^3 (a typical value for soil bulk density), and
K_d = 1,200 ml/g (1.200 m^3/kg).

By substituting above values in eqn. (10), the effective soil diffusion coefficient, D_E, for PCB is found to equal 8.4338×10^{-7} m^2/day, and with

$$t_D = l^2/D_E \tag{11}$$

it follows that t_D is about 75.5 years. In other words, a substantial period of time is required for a PCB molecule to migrate six inches in soil air in the ambient zone; the vapor retreat of chemicals like PCBs to distances such as 12 feet away from the melt during ISV simply cannot occur.

In the transition zone, however, adsorption plays a role of diminishing importance as temperature increases because adsorption is an exothermic process; therefore, the higher the temperature, the less the adsorption of organic chemicals [32] and the lower the K_d. Experiments conducted in soils at temperatures between 150 and 300°C show that higher temperatures result in less adsorption and faster desorption [33,34]. As a melt advances, temperature increases and organic chemical adsorption decreases, allowing diffusion and convection to govern chemical movement.

Summary and conclusions

The ISV mechanisms of melt production and solidification is similar to the natural reactions that create igneous rocks on earth. During ISV, heat generated by applying electrical current to soil creates a melt that can attain temperatures greater than 1,700°C (i.e. 3,092°F). Convective flow causes a continual mixing of the melt that creates uniform chemical distribution and composition within it.

When this melt cools, it forms a glass rock with a relatively uniform chemical composition and a random atomic structure that is basically the same as obsidian. The durability of ISV-derived obsidian is similar to that of granite. The mean life of the ISV-derived obsidian would be on the order of 1 million years.

In situ vitrified derived obsidian has been subjected to a variety of leach tests, including the EPA's Extraction Procedure Toxicity Test (EP Tox) and Toxic Characteristics Leach Test (TCLP). All of these tests show a uniformly low leach rate for heavy metals. Tests on ISV-derived obsidian show that its leaching resistance is superior to that of marble and common bottle (i.e. lime soda) glass.

The presence of a melt in subsoil has a substantial effect on several soil chemistry reactions and processes governing the migration and degradation of chemicals in soil. First, the number of collisions among molecules of chemicals present in the soil system will increase as soil temperature increases; as a result, the chemical reaction rate accelerates as soil temperature increases.

Second, hydrolysis reactions will occur at an accelerated rate for many organic chemicals whose reaction rates are dependent upon soil acidity. Because ISV processing decreases the soil water content in the transition zone and the dry zone without decreasing the amount of acidity present, greater acidity near soil particle surfaces should occur and cause an increase in organic chemical hydrolysis rates.

Third, during concentration diffusion, chemicals migrate from regions of higher concentration to regions of lower concentration; the greater the difference, the greater the diffusion rate. The high temperatures of the melt and pyrolysis zones pyrolize organic chemicals present in soil as these zones grow in volume and engulf soil. As a result, the melt creates a concentration diffusion gradient towards itself.

Fourth thermal diffusion will cause some molecules of the organic chemical to migrate away from the melt in an attempt to establish an equilibrium that compensates for the effects of concentration diffusion. However, vapors cannot move to cooler locations beyond the vapor point isotherm without recondensing. As a result, the ambient soil zone remains a barrier where ambient conditions control chemical migration. At the point of recondensation, concentration diffusion resumes control of chemical movement. Migration towards the melt resumes, and pyrolysis continues to lower the concentration of the organic chemical. As a result, concentration enrichment does not occur at locations cooler than the vapor-point isotherm and in the ambient soil zone.

Fifth, the migration of organic chemicals near the melt is significantly affected by gaseous convection. Water vapor is the predominant gas present within the treatment zone that acts as a carrier gas during ISV processing. Water balance measurements and findings from radio frequency *in situ* soil decontamination studies using tracers showed that water vapor and chemicals move upward to the soil surface where they are captured in the hood and treated by the off-gas treatment system. Chemicals move into the heated zone from adjacent soil outside of the heated zone; no migration of chemicals from the heated area to the surrounding soil occurred.

Sixth, the melt advances at a rate that overtakes the ability of capillary forces to move significant amounts of water, and chemicals dissolved in water, to the melt.

Seventh, in the ambient zone, adsorption is the primary process retarding the movement of many organic chemicals. However, it plays a role of diminishing importance as temperature increases because adsorption is an exothermic process; therefore, the higher the temperature, the less the adsorption of organic chemicals. As a melt advances, temperature increases and organic chemical adsorption decreases, allowing diffusion and convection to govern chemical movement.

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