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Self-ignition Behavior of Metal Hyperaccumulator Plants: Influence of Metal Content on their Thermal Stability

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The thermal stability of hyperaccumulator plant storages was investigated. Isothermal basket tests were performed according to EN 15188 on ground and sieved samples of *Alyssum murale*, containing approximately 1 %w Ni. Some plants were washed and dried to reduce Ni concentration to 0.2 %w. Tests were also performed by mixing the plants after Ni removal with iron powders to highlight the influence of metal addition. Thermogravimetric analyses and experiments in Grewer oven were run to determine the onset temperature, the combustion enthalpy and the oxidation kinetics using Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose methods. The self-ignition temperature was significantly decreased by the presence of Ni within the plants (approximately 20 K less when Ni was still present). Complementary results were obtained by mixing iron powders and plants. These trends were confirmed by the evolution of the onset temperature. They could neither be related to a porosity change, nor to Biot number modification, as the experimental thermal conductivity was only slightly affected by the presence of 1 % of metals. Frank-Kamenetskii model was applied to the various tested materials and bring out an activation energy in good agreement with that obtained by thermogravimetry. The influence of the diffusion-controlled reaction was highlighted and the influence of metal accumulation on the thermal stability of hyperaccumulator plants was demonstrated.

1. Introduction

Self-heating of bulk storages can occur when the heat dissipated at their surface is lower than the heat generated inside them by chemical (oxidation…), biological (fermentation) or physical (water condensation) phenomena (Broeckmann et al., 2016; Krause, 2016). Their thermal stability depends notably on the competition between conductive and convective transfers, i.e. Biot number. Two extreme cases can be considered: that of highly conductive metals and that of insulating organic powders. Generally, plant storages can be likened to the second case, but some plants, called hyperaccumulators, potentially contain high levels of metals. They are specifically grown in areas of metal-rich soil (e.g. ultramafic soils) with abilities to absorb metal at much larger scales than any other plant. Among them, *Alyssum murale*, known as a nickel (Ni) hyperaccumulator, has the capability of accumulating over 100 kg of nickel per hectare. Such plants can be used both for the agromining of nickel or more specifically for the remediation of abandoned and heavily contaminated soils (Van Der Ent et al., 2017). Due to their large metal contents, their chemical and thermal properties can deviate from that of other biomass, leading to potential changes in the thermal stability of their storages. The oxidation kinetics, thermal properties and self-heating behaviour were studied for the raw plants, water-washed samples, as well as mixtures of plants with a selected iron powder.

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2. Materials and methods

2.1 Samples preparation

As the initial sample contain both dried stems, leaves and roots fragments, the raw plants were crushed using a blade mill to acquire a homogenous powder sample. It was then sieved to minus 500 µm to remove large root and stem fibers. The particle size distribution of the crushed raw plants was determined in ethanol by using a Mastersizer 2000 (Malvern Instruments) (Table 1). The diameter $d_{3,2}$ is the Sauter mean diameter. The parameter d_{90}, diameter which is the intercept for 90 % of the cumulative volume, is greater than 500 µm. This can be explained by the presence of fibers having a large anisotropy. The particle size distribution observed is consistent with that of the dust generated by erosion or attrition during the processing of hyperaccumulator plants.

Table 1: Particle size distribution of sample after grinding

d (µm)	d_{10}	d_{50}	d_{90}	$d_{3,2}$
Raw plants	78.3	293.2	934.8	91.6

A fraction of sample of raw plants was water-washed several times and dried in order to lower its metal content, which was determined by Inductively Coupled Plasma Mass Spectrometry (ICPMS) after plant mineralization using nitric acid. In Table 2, it can be observed that the nickel concentration is decreased by more than 60 %. However, it should be underlined that the global metal content is decreased from 4.9 %w. to 2.3 %w. by the washing process, as several other metals were detected and quantified.

Table 2: Comparison of some metal mass concentrations for raw and washed plants

Metals (%w.)	Al	Fe	K	Mg	Ni
Raw plants	0.2	0.8	0.85	0.85	0.65
Washed plants	0.05	0.3	0.35	0.3	0.25

In order to investigate the effect of the metal presence on the self-ignition characteristics of the hyperaccumulator plants, a portion of the washed plants was mixed with pure iron powder. Iron was chosen instead of nickel due to the toxicity of nickel particles, and to its rather large mass content in the raw plants. The mean particle size of iron (60 µm) was selected to be consistent with the d_{10} of the ground raw plants. The plants were mixed with iron particles using a chaotic stirrer (Turbula) to ensure homogenous mixtures.

2.2 Thermal properties of the powders

Through Biot number, the thermal conductivity λ is a critical parameter in the investigation of self-heating. It was determined using a CTi thermal conductivity analyser (CTherm) both for the raw plants and for washed samples. Tests were carried out on a thin layer of powder placed onto a sensor in which a known current is applied to a heating element. It appears that the thermal conductivity remains unchanged before and after the water-washing, reaching 0.054 $W.m^{-1}.K^{-1}$.

In order to study the effect of metal content on the thermal conductivity of the hyperaccumulator plants, tests were performed on samples with iron mass concentration up to 30 %w. (Figure 1). Increasing the metal content up to 5 %w. does not change significantly the mixtures thermal conductivity, which is consistent with the results obtained on raw and washed plants. However, for larger metal concentrations, the impact on the thermal conductivity cannot be neglected as it increases by more than 20 % when reaching 30 %w. iron content. This evolution is well represented, on this concentration range, by the classical Maxwell model (Bowes, 1984) originally designed to predict the effective thermal conductivity of composite materials and modified for porous materials (Figure 1).

The thermal properties of the plants were also studied by determining their onset temperature and heat of combustion using a Grewer oven. 8 mL mesh baskets were filled with powders for measurement and the latter is used with an alumina reference inert sample. Each mesh basket contains a thermocouple to monitor temperature evolution. The oven is subjected to an air flow stream to allow oxidation of the materials. The oven is heated linearly at 4°C.min^{-1} until a maximum temperature of 400°C. The determination of the onset temperature of ignition is deducted from the progression of temperature with time, and the integration of the temperature peak as a function of time leads to the estimation of the heat of reaction. Copper sulphate pentahydrate samples were used for calibration.

Thermogravimetric analyses (TGA) were performed using a Setsys Evolution 1600 (Setaram) thermobalance. An air flow of 200 mL.min^{-1} was used as the carrier gas. 60 mg samples were heated to various maximum temperatures (250 to 500°C) using a constant heating rate (5 K.min^{-1}) and other experiments were performed with various heating rates (2, 5, 10 and 20 K.min^{-1}) to reach a constant maximum temperature (500°C). During heating, both the mass of the sample and the furnace temperature were recorded. Flynn-Wall-Ozawa, Kissinger and Kissinger-Akahira-Sunose methods (Vyazovkin, 2015) were applied to determine the kinetics parameters of plants combustion, assuming a single step mechanism.

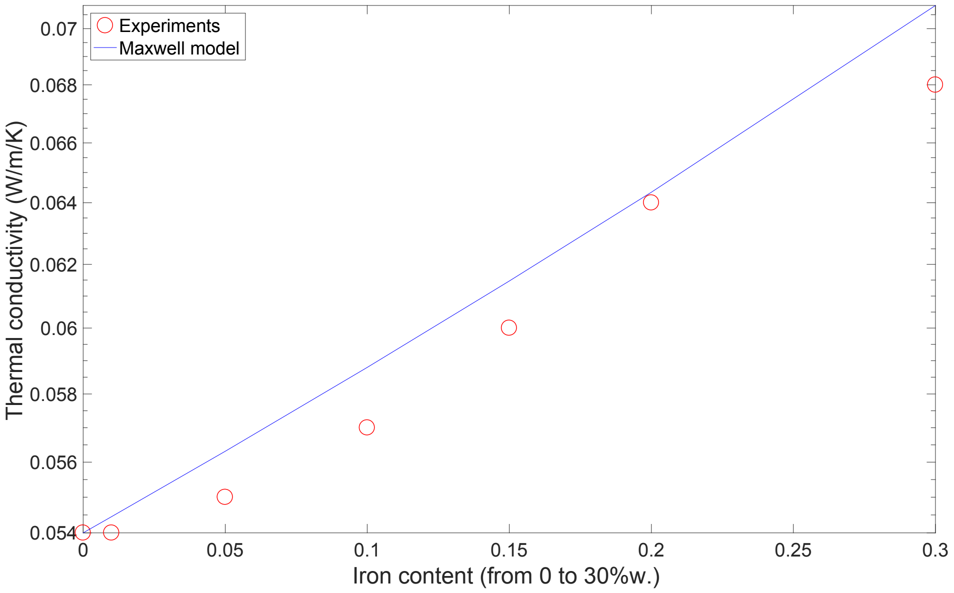

Figure 1: Thermal conductivity of hyperaccumulator plants/metal mixtures, as a function of the iron content

2.3 Self-heating tests

Isothermal basket tests were carried out according to EN 15188 (2007), in order to determine the self-heating characteristics of the organic powders and the critical ignition temperature for a series of various sized baskets. In addition to the thermocouple placed in the center of the sample, two others were located at its surface and at a third of the height in order to identify the location of self-heating and its dependency on the oxygen content. The ignition criterion is validated if the powder temperature exceeds that of the oven by 60 K within the 24 h testing window. When ignition takes place, the tests are repeated at a lower temperature until no ignition is observed. This procedure is applied on the minimum of 3 various sizes of baskets among 15.6, 125, 1000 and 2744 cm^3.

Frank-Kamenetskii theory was used to evaluate the self-heating behavior of the powder samples. Provided the mechanism is unchanged with size progression (even if limitation due to oxygen diffusion within the powder beds has to be kept in mind), the theory is considered as valid to assess the critical ignition temperatures (T_A) for large quantities of material (Bowes, 1984). One of the numerous assumptions made for applying this model is an infinite Biot number Bi, or at least, Bi should be greater than 30. It is worth noting that for finite values of the Biot number, the approach developed by Barzykin et al. will be preferred (Bowes, 1984). By using a critical Frank-Kamenetskii dimensionless parameter δ_c set at 2.569 (Bowes,1984) and by tracing $\ln\left(\frac{T_A^2\delta_c}{r^2}\right)$ as a function of 1/T for various sizes r (half-length of the cube) of powder piles, the activation energy of the combustion reaction can notably be estimated.

3. Results and discussion

3.1 Oxidation kinetics of hyperaccumulator plants

Tests performed with the Grewer oven allow the determination of the onset temperature for the combustion reaction of the raw plants, i.e. 240°C (Figure 2). It appears that when the total metal content of the plants drops from 4.9 to 2.3 %w. (after water-washing), the onset temperature tends to increase up to 255°C. However, the addition of 5 %w. Fe to the washed plants decreases the onset temperature approximately to its initial value. Then, the presence of metal seems to promote the oxidation of the biomass. Nevertheless, it is worth noting that these tests conditions do not correspond to those encountered during the storage of the plants, as an air flow fluidizes the dust and avoid the oxygen diffusion limitation which usually occurs during large storages self-heating. A secondary reaction can be observed for both raw and washed plants, but is not visible for plants with iron. The heat of reaction, which is proportional to the surface area of the peak, varies by more than 30 % between raw and washed plants. Differential scanning calorimetry tests will be performed to investigate this trend.

A slightly lower onset temperature of 220°C was obtained by thermogravimetric experiments performed on raw plants. Again, the air diffusion within the powder sample is different during TGA and Grewer tests. Thermogravimetric analyses were first conducted using a constant heating rate and the time versus conversion curves were fitted using relationships representing the various reaction steps developed in the shrinking core model. Two regions of varying gradient can be identified on each curve. In the 0 to 0.45 range of conversion, the combustion is limited by the chemical reaction, and thus the reaction rate is proportional to the available surface of unreacted core. Then, the combustion becomes controlled via the diffusion of oxygen to the unreacted plant, which is likely to occur during the self-heating of large storages.

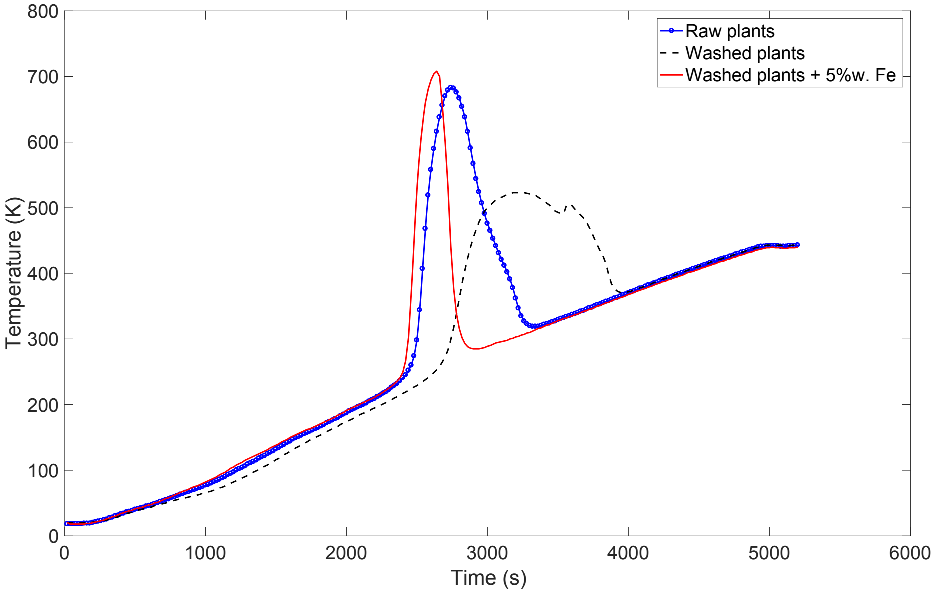

Figure 2: Influence of the inherent metal content or of metal addition on the thermal behaviour (Grewer test)

The differential mass loss thermograms obtained at variable heating-rates also show three regions related to the dehydration of water, the active oxidation which begins at 220 to 240°C and levels off at around 430°C, and the passive oxidation governed by oxygen diffusion. For the raw hyperaccumulator plants, the average weight of the final solid residue is around 6 %w. of the original sample, for all heating rates. Furthermore, the kinetics parameters obtained from the Kissinger method are 129.1 kJ.mol^{-1} and 1.8x10^{11} for the activation energy and the pre-exponential factor respectively. The kinetic parameters determined for the Flynn-Wall-Ozawa (FWO) method and the Kissinger-Akahira-Sunose (KAS) method were determined for conversion values ranging between 0.1 and 0.6, which mainly corresponds to the chemical reaction limitation region. The activation energy for both the FWO and KAS methods shows a changing value across conversions which indicates the likelihood of a more complex multi-step mechanism occurring during oxidation. The ranges of activation energies are around 107.7 to 150.3 kJ.mol^{-1} and 103.1 to 157.0 kJ.mol^{-1} for FWO and KAS, respectively. It is also important to note that the assumption of an unlimited amount of reactants, done with such methods, is certainly valid for self-heating in industrial conditions, but is subject to caution when using thermogravimetric analyses (samples of a few milligrams).

3.2 Thermal stability of hyperaccumulator plants

The results of isothermal baskets tests carried out for the raw hyperaccumulator plants are shown in Figure 3 for four basket sizes. The critical self-ignition temperature, which is the lowest temperature for which self-heating occurs, decreases as the sample size increases, along with an increase in the ignition delay time (from 50 to 400 min). It should be noted that, in the case of the two largest baskets, the ignition occurs often at the third of the height of the cube, which confirms the presence of limitation due to oxygen diffusion. Tests were also performed on the washed plants, having a lower metal content. It appears that the thermal stability of these samples was improved with regard to the raw plants (Figure 3). For instance, the self-ignition temperature increases from 210°C to 230°C for the 15.6 cm^3 basket, when the plants are washed. Moreover, the influence of metal removal seems to be more significant for smaller than for larger storages, where the oxygen diffusion limitation is more important. It should be noticed that the critical temperature is approximately 100°C for storage dimensions (half-length of the cube) of 1 meter.

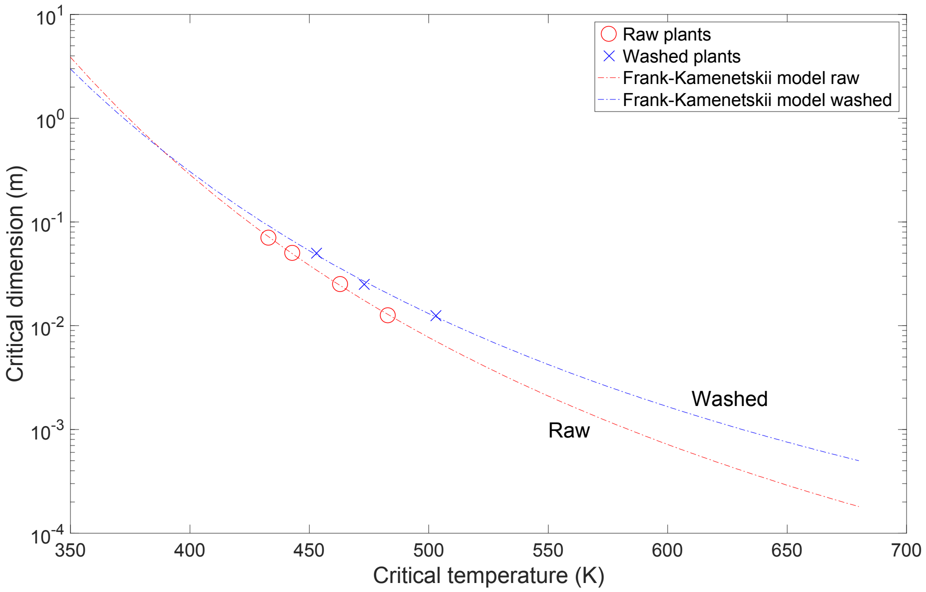

Figure 3: Thermal stability of raw and washed hyperaccumulator plants

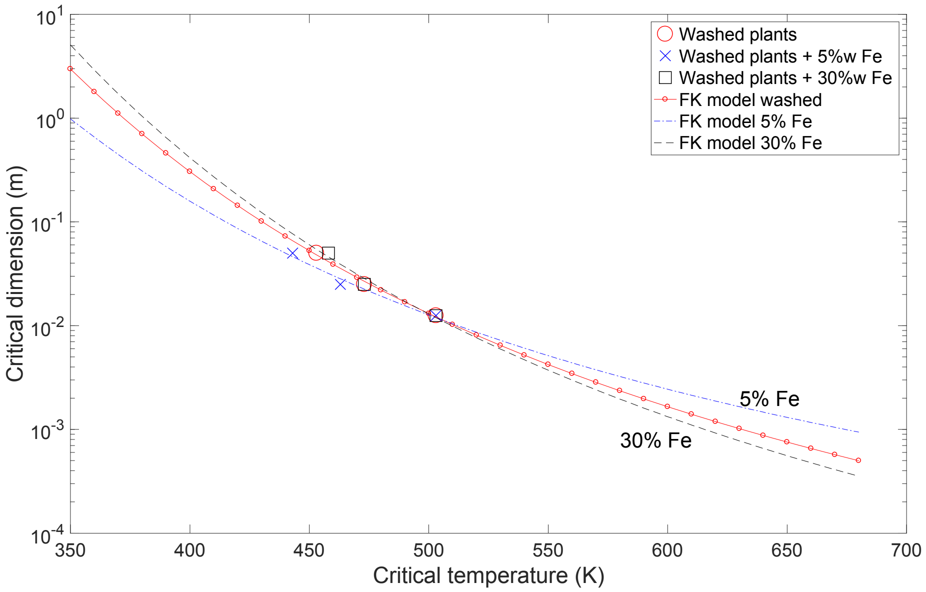

Figure 4: Influence of metal addition on the thermal stability of hyperaccumulator plants

The results of critical self-ignition temperatures can be interpreted with Frank-Kamenetskii theory. The activation energies are 127.6 kJ.mol^{-1} and 112.2 kJ.mol^{-1} respectively for the raw and washed plants. These values are consistent with the activation energies determined by thermogravimetric experiments, as well as with data from the literature for various similar biomass samples (Bowes, 1984; Sonobe and Worasuwannarak, 2008). The activation energy decreases significantly with the removal of metals from within the plant. Metals, especially nickel, being used as catalysts, the reverse trend could have been expected (Tagawa and Rose de la Rama, 2013). However, it should be stressed that the metals present in the plants do not exist in a metal form, but as a part of a complex forming the cell tissues. Moreover, the plant structure may be altered by the water-washing process. Finally, it should be kept in mind that these activation energies have been determined for a single step combustion mechanism, which is obviously not the case as shown by Grewer oven results and thermogravimetric tests.

3.3 Influence of metal addition on the self-heating of hyperaccumulator plants

Figure 4 shows that the addition of iron particles to hyperaccumulator plants does not affect significantly their self-heating behavior. The addition of 5 %w. iron powder seems to decrease slightly the thermal stability of such mixtures with regard to the washed plants. However, this is not the case anymore when 30 %w. iron is added. The application of Frank-Kamenetskii model to 5 and 30 %w. iron mixtures leads to the determination of their activation energies, i.e. 91.3 and 122.8 kJ.mol-1 respectively. The addition of a small amount of iron seems to reduce the activation energy, whereas a larger content does not modify significantly this parameter. Various potential influences must be taken into account in addition to the catalytic effect of iron, such as the variation of the storage porosity and the increase of the powder conductivity (Figure 1). Indeed, an augmentation of the storage conductivity can enhance the heat dissipation and increase its thermal stability.

4. Conclusions

This preliminary study dealing with the thermal stability of hyperaccumulator plant storages demonstrates that the metal content has clearly an influence on their self-heating behaviour. Indeed, lowering the metal content of the plants by washing them with water tends to increase their thermal stability. It appears that this effect is probably not due to the modification of the thermal transfer properties as their thermal conductivity is not significantly affected by the presence of less than 5 %w. of metals. Moreover, the porosity of raw and washed powder beds is unchanged. Furthermore, the onset temperature is lowered by 20 K and the activation energy modified by the presence of metals within the plants. As a consequence, a chemical effect of the metals accumulated within the plants cannot be neglected (nickel, iron, magnesium…). The influence of oxygen diffusion limitation was highlighted and average activation energies of 120 kJ.mol^{-1} were determined in the case of a single step mechanism. It was also demonstrated that the addition of 5 %w. metal powder does lead to the same effect than 5 %w. of metal present in the plants in the form of a complex. Finally, the addition of large amount of metal powder modifies the thermal conductivity of the mixture and tends to improve the heat dissipation.

Questions have to be raised about the legitimacy of the Frank-Kamenetskii method for predictions of real sized stockpiles of biomass, especially when the Biot number is rather low, because this model does not take into consideration reactant consumption and the multiple-step mechanism of biomass oxidation. As a consequence, the results obtained during this study will be used to validate a two-dimensional axisymmetric model initially developed for metal/inert mixtures (Dufaud et al., 2014). These first results will serve as a basis for a global risk analysis of the agromining process.

Acknowledgments

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