XRF – New Applications in Sensor-Based-Sorting Using X-ray Fluorescence

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Abstract

In recent decades, waste management has developed from simply waste disposal toward waste treatment, waste recovery and recycling. Even though waste collection has reached a high standard and many different waste streams are collected separately, an after-treatment is required. Each waste stream is more or less polluted with undesired types of materials making the treatment of collected waste in certain plants obligatory. BT-Wolfgang Binder GmbH is a general contractor specialized in mineral and environmental technology and develops different sensor-based sorting machines with technologies such as Near Infrared Spectroscopy, Infrared-Transmission and Line Scan Cameras as well as X-ray fluorescence analysis.

The REDWAVE XRF system is capable of identifying and separating various types of materials by measuring differences in their elemental composition. When materials are exposed to electromagnetic radiation (X-rays), electrons are ejected from the atomic shell and the resulting free spots are occupied via an electron transfer from outer shells. This electron transition causes the emission of radiation (photons) – the so called secondary X-ray fluorescence radiation – and is characteristic for each transition and each element. By measuring that radiation with special detectors, it is possible to determine the elemental composition of the in-feed material. The sorting criteria can be based on one element, multiple elements or a ratio of two elements.

In general all solid materials containing a specific and characteristic element can be analysed. The technology of X-ray fluorescence is therefore not limited to one material class or application but can be used in a wide variety of fields. Besides resource recycling it can also be used for sorting for various materials such as ores and mineral and as online quality control

1. Introduction

In recent decades, waste management has developed from simply waste disposal toward waste treatment, waste recovery as well as recycling. Material flow aims to make the processing of waste economical and ecological. As such material flow management attempts to achieve environmentally-friendly and resource-conserving production, reuse of recyclable materials, and targeting to minimize emissions. Recycling economy and cleaner production make the use of secondary resources possible and hence, save primary resources, energy and prevent waste. Even though waste collection has reached a high standard, and many different waste streams are collected separately, an after-treatment of every single waste stream is obligatory. In the infancy of waste management, only treatment of homogenous waste streams was possible. However, increasingly sophisticated technologies have made the sorting of heterogeneous waste streams possible. Due to the extinguishing of primary resources, increasing prices for raw materials, rising energy prices and reinforced laws regarding landfill prohibitions and recycling rates, the future promises more and more applications for sensor-based sorting systems. Near Infrared Spectroscopy, Infrared-Transmission, Line Scan Cameras and X-ray Fluorescence are only a few examples of sophisticated sensor-based sorting-systems. The newest development is a sensor-based sorting system based on X-ray fluorescence. This technique was developed by BT-Wolfgang Binder GmbH in collaboration with Olympus Innov-X Systems.

2. Theoretical Background

2.1. X-Rays

X-rays, discovered by W.C. Röntgen in the year 1895, are high energy, electromagnetic waves with a wavelength in the range of 0.001 nm and 80 nm, corresponding to energies between 1.2 MeV and 15 eV. In the spectrum of electromagnetic radiation, X-rays are between UV-light and Gamma-rays. Electromagnetic waves can also be considered as a *stream* of particles (photons), which travel with the vacuum velocity of light. The particle´s energy E is proportional to its frequency f with the proportionality factor h for Planck´s constant. The energy can be calculated from the Planck-Einstein equation:

$$E = hf[ev]$$

The intensity of X-ray radiation (and radiation in general) relative to a distance can be described by the inverse-square law. The intensity I (or power per unit) varies inversely with the square of the distance r^2 from the source.

$$I \propto \frac{1}{r^2}$$

An increase in the distance by a factor of two causes an intensity-drop to one fourth and similar, by lowering the distance to one half, the intensity rises by the factor of four. Hence, distance from X-ray source to sample but also from sample to detector is crucial in X-ray fluorescence analysis.

2.2. Physical Principle of X-ray fluorescence

The Bohr model in atomic physics depicts the atom as a small, positively charged nucleus surrounded by electrons travelling around the nucleus on orbitals. Electrostatic forces provide attraction for travelling electrons. If X-ray radiation (e.g. from X-ray tubes) is incident on matter and if the energy of this incident radiation is high enough, more precisely exceeds the bond energy of electrons on the orbital (ionization energy), emission of electrons due to the photoelectric effect takes place. In the photoelectric effect, electrons are emitted from matter as the consequence of their absorption of energy from photons, whereby this photon is annihilated. The quantity of absorbed energy is equal to the bond energy of the emitted electron. The remaining energy $E_{kin,Photo\text{-}electron} = E_{Photon} - E_{Binding}$ is carried by the emitted (photo-) electron. This mechanism is certainly only possible if the energy of incident radiation is greater than the ionization energy of the electron. This process creates vacancies on the orbitals and the atom gets ionized. Such vacant spots are refilled by an electron transition from an outer orbital and the atom relaxes. Since the bond energy of outer orbital electrons is always higher than inner ones, energy is obtained during the electron transition. This energy can then be emitted as secondary fluorescence radiation (The so called Auger-effect is also possible and is competing the effect of X-ray fluorescence). This secondary X-ray radiation is characteristic for each element and characteristic for each individual electron transition. By measuring this radiation with special detectors it is possible to determine the elemental composition for the targeted material. Figure 1 gives a graphical explanation of the physical principle of X-ray fluorescence.

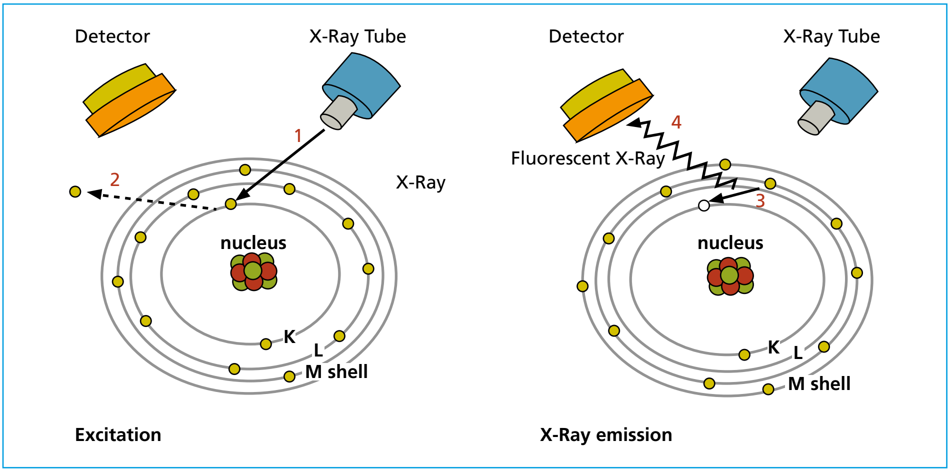

Figure 1: Physical Principle of X-ray Fluorescence

The excitation of matter with X-rays (1) and as a consequence the emission of electrons (2) causes the creation of vacancies and the atom becomes ionized. Then, within ps (picoseconds) the excited atom relaxes (reaches ground state) by refilling the vacancy from an outer shell (3). The due to this process emitted radiation (4) is captured by special detectors and makes qualitatively and quantitatively analysis possible.

3. X-ray Fluorescence Sorting Machine

The REDWAVE XRF is a sorting machine to determine the elemental composition of various materials with X-ray fluorescence. Based on this analysis objects with specific elements are detected and can be separated from the material stream. With the sorting systems, materials such as glass, ceramics, metals, minerals, plastics can be treated.

Figure 2 shows a cross-section schematic of the sorting system.

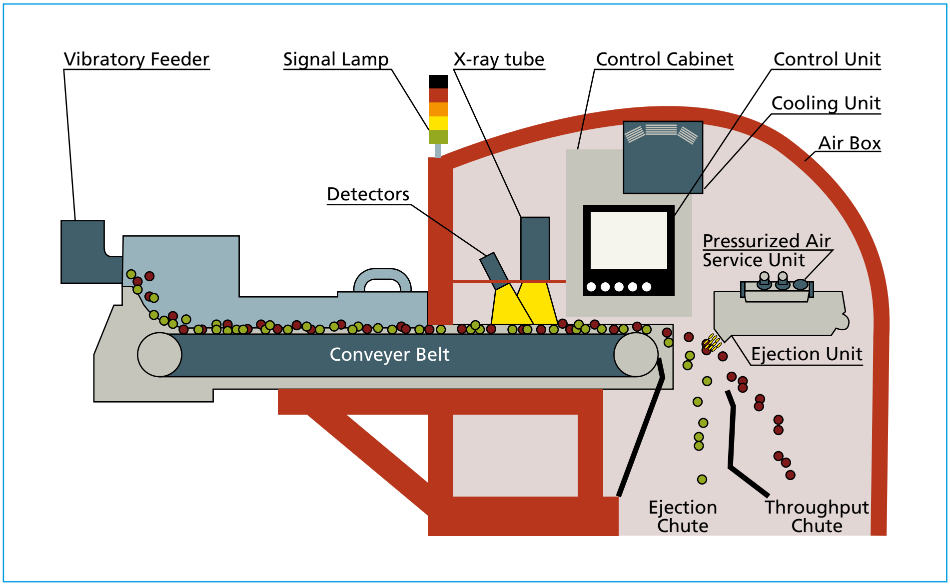

Figure 2: Schematic Drawing XRF

Sorting material is constantly fed over the entire sorting width of a conveyer belt by a vibratory feeder. Material samples are accelerated, separated and transferred toward detection area. The separation of the material on the belt is done by a difference in speed of vibratory feeder and conveyer belt. The detection is conducted as mentioned above based on X-ray fluorescence, and consists of two main parts, X-ray source and detector. The X-ray tube generates primary X-ray radiation that excites the material, which then emits secondary X-ray fluorescence radiation. These secondary X-rays are captured by special detectors. The detector signal is constantly evaluated and compared to a set threshold. The XRF sensor then performs an ultrafast elemental analysis, regardless of an object´s physical properties such as thickness, colour or the presence of labels or other impurities. If the chemistry of a material meets the set ejection criteria a signal is sent to the ejection unit. This unit is composed of high speed valves and air jets, operated by compressed air. If the set sorting criterion is met air jets are activated to reject selected material.

A photograph of commercially used sorters can be seen in Figure 3.

Figure 3:

Commercially used XRF-system (without vibratory feeder)

Sorting criteria can be based on one element, multiple elements or a ratio of two elements. For instance, the separation of leaded glass and glass ceramics from a recyclable material stream of recovered glass, the elements lead, zirconium and zinc are used simultaneously. While for sorting brass and stainless steel, a ratio of two distinguishing elements is used.

4. Practical Application

In general, all solid materials containing a specific and characteristic element (or elements) above the detection limit can be detected and separated with the sorting system. The technology of X-ray fluorescence is therefore not limited to one material class or application but can be used in a wide variety of fields. Areas of application for the sorting technology include:

- Glass: Separation of leaded glass and glass ceramics, sorting of CRT glass
- Metals: Sorting of stainless steel (e.g. 1.4571 and 1.4301), non-ferrous metals (e.g. brass, bronze, Cu, Zn), discarded metals etc.
- Ores: Sorting of ores with different content of metals, separation of ores polluted with objectionable inclusions (e.g. mercury) etc.
- Minerals: Sorting of different minerals according to purity grade, separation of minerals polluted with objectionable inclusions
- Plastics: Colour independent separation of PVC- under development, separation of brominated plastics
- Electronic scrap: Separation of electronic scrap coated with bromine and/or cadmium in shredded electronic scrap, enrichment of with valuable metals coated electronic scrap
- Residues: Separation of any valuable metals in residues e.g. separation of gold and silver in slag of (waste) incineration plants
- Quality control: The sorting system is also applicable as online quality control in the areas mentioned above as well as where a characteristic element is existent. According to requirements, different elements as search key can be adjusted. These elements are continuously identified, evaluated and then recorded, giving assurance of a quality material.

Following gives some examples for the use of an XRF-sorter:

4.1. Glass Sorting

As mentioned previously, the sorting system is versatile, and can be successfully implemented for a variety of applications. A for years existing application is glass sorting, more precisely the separation of leaded glass and heat resistant glass (glass ceramics) out of a recyclable material stream of recovered glass.

Glass, one of the oldest materials used by human beings, is a mass product of our society. Since the 1970´s, glass is collected and recycled in many countries worldwide. Hence, the consumption of quartz sand, the primary resource in glass production, can be reduced. Furthermore and an even greater benefit is that the high energy consumption at the glass production process can be reduced. Depending on the colour of the glass, between 60 % (flint) and 90 % (green) recovered glass cullet is being blended with virgin material during the production process. Glass recycling is a prime example of modern cleaner production. Since neither collection is perfect, treatment of collected waste glass is essential. Impurities in collected glass may be wrong colours, metals, organics, the so called CSP (ceramic, stone and porcelain) and also incorrect types of glass. The latter may include special-purpose glass, laboratory glass or heat resistance glass (out of microwaves, ovens etc.), and glass containing additives such as lead.

The current state-of-the-art in glass sorting uses crusher/sieves, magnetic separator and sensor-based sorting technologies such as Infrared-Transmission and Line Scan Cameras. However, due to foreseen problems with heat resistant glass (glass ceramic) and leaded glass, the identification and separation of both became necessary. Heat resistant glass leads to inclusions during the glass production process, resulting in products which are unusable due to residual stresses which result in cracks. Lead is toxic and hazardous to the environment and has therefore (according to the precautionary principle) been regulated by the EU to a content of 200 ppm (parts per million). The limit value in the US is even lower with 100 ppm. The use of X-ray fluorescence implemented in the sorting system makes reliable separation of heat resistant glass and leaded glass possible.

The separation of heat resistant glass and leaded glass in the recovered glass stream is done by simultaneous detection of zinc, zirconium and lead. Both impurities are separated from the main stream in one sorting step. Other sorting techniques using camera-technique require two different machines for the same task. Additionally to above mentioned elements, it is also easily possible to add further elemental criteria (present in impurities) making the sorting system versatile and easy to update. As the extent of impurities in the input stream is low, the ejection follows the principle of negative-sorting.

4.2. CRT glass sorting

Apart from glass sorting the system can also be used to separate CRT glass. A cathode ray tube generally consists of two glass types, funnel and panel. Whereby panel (consists strontium) which is used for the front part of a CRT is (in general) lead free, funnel consist of up to 15 % or more lead. The sorting criterion is based on both strontium and lead. Using the XRF-sorting system it is possible to create two products, funnel and panel.

4.3. Electronic Scrap – Precious Metal Sorting

In this application, the sorting task is the detection of various (precious) metals in a mixed input stream of electronic scrap. Electronic scrap consists of various metals pure or in alloys that can be separated in clean fraction using XRF-technologie. The separation is done step by step, meaning only one element at time but also more than one element can be detected simultaneously. However, the exactly separation task certainly depends on several factors such as the content of material to be separated in the input stream, presence of elements, elements to be detected etc. In Figure 4 some examples of electronic scrap can be seen.

Elements to be detected:

Zinc – Nickel – Copper – Iron – Bromine – Molybdenum – Lead – Tungsten – Tantalum – Silver

Figure 4: Examples of E-scrap

4.4. Separation of Brominated Plastic

The separation of brominated plastic from an input stream of shredded plastic is the sorting task at this application. Bromine is widely used as flame-retardant in various electronic devices. The plastic comes from shredded housings such as PCs, laptops, screens or other electronic devices and is very heterogeneous in composition. The sorting system makes it possible to generate a bromine free product by separating all brominated plastic from the input. The created bromine free product can be recycled. Separation of brominated plastic will be a promising use for the XRF-system once regulations have been set by the EU respectively the governments. In comparison to NIR- technique XRF is independent on colour and surface, hence making the detection of black plastics possible.

4.5. Separation of Nonferrous Metals

The sorting system can be used for the detection and separation of various metals. An example is the separation of copper, brass and stainless steel in an input of several metal constituents (see Figure 5 for clean metal fractions). This is done in a step by step separation of mentioned metals resulting in clean fractions of copper, brass and stainless steel. Hereby

Elements to be detected:

Copper – Brass – Stainless Steel

Figure 5: Clean Metal Fractions

created clean metal fractions are high of value and can be recycled. All sorting steps can be done with the same sorting machine by using various sorting programs with different ejection criteria. Furthermore, further necessary elements can be easily implemented at the existing system.

4.6. Treatment of Aluminium

Similar to above mentioned separation of nonferrous metals in a metal fraction is the separation of the very same metals to create clean aluminium. Depending on the origin of the aluminium, impurities can among others be copper, brass, zinc, lead and stainless steel. The separation of all non-aluminium pieces is done in one step, however, an after-treatment of the separated fraction (copper, brass, zinc, stainless steel etc.) into clean fractions can be performed as well with the same sorting system but using another sorting program. The big advantage using the XRF sorter is the possibility of colour independent identification. Treatment of aluminium and aluminium sorting e.g. 6063 is a promising application of the XRF-system.

4.7. Mineral/Ore Sorting

The XRF sorter is not limited to resource recycling and can also be used for mineral sorting. At mineral sorting the application can be divided into two main parts. First, sorting of different minerals according to purity grade respectively the presence of certain elements. This is done by simply detecting wanted element(s). Secondly, the sorting system can be used to separate unwanted inclusions in an input stream. A typical inclusion may be cinnabar (Hg-suflide). The machine detects the mercury and specifically separates contaminated ore pieces. A sorting machine for separating cinnabar inclusions and the after-treatment of ore is in commercial use.

4.8. Online quality control

Beside the separation of impurities or the sorting of resources the sorting system can also be used as online quality control. By measuring a bypass stream or the total stream of a given input wanted elements are constantly measured and evaluated giving assurance of the quality. This can in general be used for all above mentioned applications and where one characteristic element or elements need to be analysed.

4.9. Conclusion

Besides the application of glass sorting, the sorting system is in commercial use in fields such as electronic scrap sorting, metal separation, precious metal separation and mineral sorting. Most are used for glass sorting but particularly the last year shows that this technique is not limited to glass sorting but can be used for almost any material. Many new applications in different areas came up in the past year giving the XRF-technique a promising future. Depending on the sorting task, different elements are set as sorting criteria and can be separated from the input stream simultaneously or step by step. The sorting system is not limited to resource recycling but can be used for various sorting tasks or online quality control.

5. Summary

The treatment of waste is getting more and more important in our society requiring steady development of more advanced sorting techniques. BT-Wolfgang Binder GmbH is a general contractor specialized in mineral and environmental technology and has developed different sensor-based sorting machines with technologies such as Near Infrared Spectroscopy, Infrared-Transmission and Line Scan Camera. The most recent development is a sorting system based on X-ray fluorescence. The sorting system is capable of identifying and separating various types of materials by measuring differences in their elemental composition. When materials are exposed to high energy, electromagnetic radiation (X-rays), electrons are ejected from the atomic shell. The resulting free spots get filled up by an electron transfer from outer shells, causing the emission of radiation (photons). The radiation produced is characteristic for each element, by measuring it with special detectors, it is possible to determine the elemental composition of materials. The sorting criteria can be based on one element, multiple elements or a ratio of two elements.

In general, all solid materials which contain a characteristic element can be analyzed and separated. The technology of X-ray fluorescence is therefore not limited to one material class or application but can be used in a wide variety of fields. The separation of heat resistant glass and leaded glass out of a recyclable material stream of recovered glass is one such well-established example. However, due to the demand more and more applications arise. Besides glass sorting, the sorting system is capable of sorting various materials such as metals, ores and minerals, plastics, electronic scrap among others. Furthermore, the sorting system is also capable as online quality control in the above areas, as well as where characteristic elements existent.

6. References

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