The stability of sodium percarbonate is compromised by a small amount of metal ions in a packaging material

Instruments to which this note applies: I-Cal Flex

Prepared by: Lars Wadsö

Target use: Stability, compatibility, sodium percarbonate

Introduction

The term *compatibility* means that different elements in contact with each other work well together, and it is a term commonly used in chemistry to denote that chemicals and materials can be used in contact with each other. Conversely, chemical incompatibility occurs when substances or materials in contact with each degrade faster than they would have done on their own. The term incompatibility can be used both for cases where reactions between chemicals cause hazards like explosions and fire, and for cases where the degradation is slower. In the latter case, the process does not pose any immediate hazards, but one (or both) of the substances or materials will slowly degrade and lose its desired properties. Common examples of incompatibility are when:

- A drug compound is degraded in contact with other components in a tablet formulation.
- A packaging material promotes the degradation of a packed product.

In general, compatibility testing by isothermal calorimetry is made by comparing the heat production from the individual compounds, and from the compounds together. If we call the two compounds A and B, we would make measurements on A, on B, and on A+B. If the measurement on A+B shows higher heat production than the sum of the heat productions from A and B, this is an indication that a reaction takes place and that we have a case of incompatibility. In the case presented in this application note, the amount of B is small compared to the amount of A, and the effect we are looking for is of a catalytic nature. In that case we may assume that the small amount of B will not produce any measurable thermal power on its own, and then only measure two combinations: A and A+B. This is illustrated in Fig. 1.

Sodium percarbonate (SPC) is used as a bleaching agent in powder based laundry products and its stability depends on several factors, most typically humidity and the presence of some metal ions, like copper. Keeping it dry and away from sources of metal ions is therefore important for the stability of the product. SPC can also show incompatibility with other substances used in powdered detergent formulations, as shown in reference [1] on SPC-zeolite compatibility.

Note that:
- For a comparison between the results of A, B and A+B to be valid, the results from the different measurements must be scaled in proportion to the relative mass of each compound in the final product.

- In some instances, it is not trivial to get different solid substances and materials in close contact with each other. Typically, the substances or materials are finely divided, placed in the calorimetric vial and mixed by shaking. For a more intimate contact the components can also be pressed together.
- An increased heat production from the combination of the substances/materials indicates incompatibility, but the opposite – no increase in heat production – is not necessarily proof that the materials are compatible. Reactions with a low and undetectable heat production may still cause incompatibility problems.
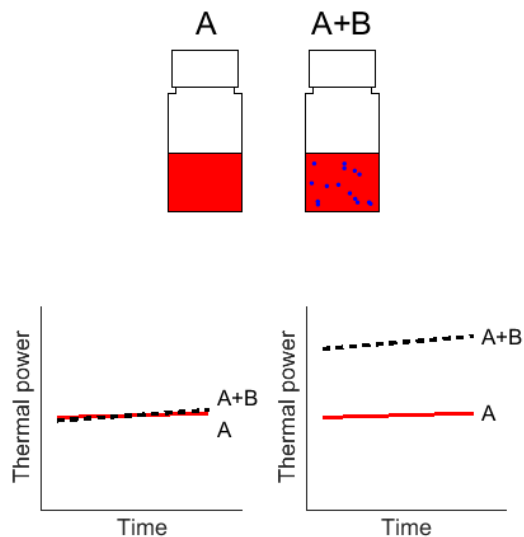

Fig. 1 – Compatibility testing of how a small amount of one substance (B) influences another substance (A). Top: schematic of the two test vials. Bottom: schematic examples of when no incompatibility is detected (left) and when there is a clear indication that B causes A to degrade (right).

In this application note we show the principle of calorimetric compatibility testing by investigating the compatibility between SPC and paper. This is a real world test example of relevance, since paper-based boxes are commonly used for SPC containing products. The test protocol consisted in preparing paper samples with and without copper ions, and then measuring the heat production when SPC is in contact with each of the samples, as outlined below.

Materials and methods

Two paper materials were used. Both were based on the same standard white copying machine paper:

Paper A - Treated with a weak solution of $CuSO_4$.
Paper B - Untreated

Both papers were dried at 50% RH before the measurement.

The source of SPC use in this example was a product marked as incorporating ">30% oxygen containing bleach compound" (which typically means that it contains approximately 65% sodium percarbonate). The remaining 35% are typically mainly sodium carbonate, but also surfactants, enzymes, fragrances, etc.

Four samples were made by taking 16 g of the SPC product. Thermal powers of the product itself were measured in each of the four samples, after which pieces of paper cut into 2 mm × 2 mm pieces were added to some samples as the measurement continued. After the paper had been added, the vials were shaken manually for 45 s. The four samples were:

1. No paper added.
2. Paper A added (32 $\mu g_{Cu}/g_{SPC}$).
3. Paper B added.
4. Paper A added (16 $\mu g_{Cu}/g_{SPC}$).

The measurements were made at 40 °C in a Calmetrix I-Cal Flex using standard 20 mL polyethylene (PE-HD) vials. The calorimeters had previously been calibrated electrically and baselines were taken after completion of the measurements.

Results and discussion

Figure 2 shows the result normalized by mass of the SPC product. It is clearly seen that paper A (treated with copper sulfate) increases the thermal power, and that a higher increase is seen for the sample with more paper (more copper).

However,Fig. 2 also shows that there is an increase in thermal power for the paper without added copper ions. This is probably an effect of the moisture content of the paper (an ordinary paper contains 5-10% absorbed moisture at 50% RH), as water is a well-known enhancer of SPC degradation [2].

Notes on proper interpretation of early parts of the calorimetric measurement

Many real world experiments present imperfect situations or results that are influenced by experimental protocols. Calmetrix application notes always show real, unaltered, experimental results, including imperfections. In this case, when the samples are initially introduced into the calorimeters, the early part of the signal seems abnormal, as it first comes from the negative side, then peaks above the final value, before settling to a quite constant value. The reason for the peak is that in this experiment, the calorimeters were not well balanced. All calorimeters had references for samples with heat capacities of about 31 J/K, which probably is significantly higher than the heat capacity of 16 g SPC. When

the vials were inserted into the calorimeters, the vials had a lower temperature than the calorimeters, which translates into the initially negative values of thermal power. However, the final approach to steady-state is influenced by the sample-reference balance, which in the present case results in a peak in each measurement. This peak does not represent heat production in the sample, but is an artifact caused by the non-balanced system, and would have been absent if the calorimeters had been well balanced. Nevertheless, the stable thermal powers after the peaks are true thermal powers and can still be used to interpret the effect of copper ions on SPC degradation.
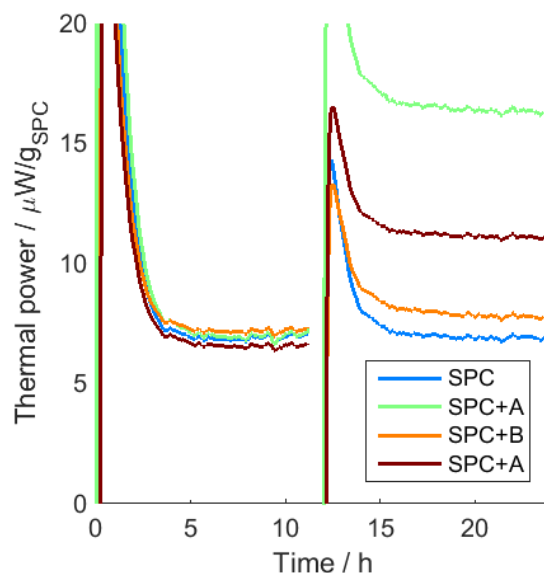

Fig. 2. – Results from measurements on SPC (first 10 h) and SPC with added paper materials (after 12 h).

Having two different additions of paper B, with aclear difference in the effect on SPC degradation, shows that it is often times possible to get a lot of information from only isothermal calorimetry, if several different measurements are made.

Also note that before reaching a conclusion, in this case, it would be important to not only run samples with SPC and paper B. For a more complete understanding of what influence paper B has on SPC degradation, and to assess he influence of water, we first may want to run SPC, and then SPC with paper B, and finally SPC with a paper that is known not to increase degradation

References

1. Johansson, C., P. Pekonen, and D. Forsström, The long-term stability of sodium percarbonate in presence of zeolite as measured by heat flow calorimetry. Tenside Surfactants Detergents, 2007 44 4 210-217.
2. Brundu, M. and V. Guida. *Modeling the chemical decomposition of sodium carbonate peroxyhydrate*. in *COMSOL Conference*. 2012. Milan.