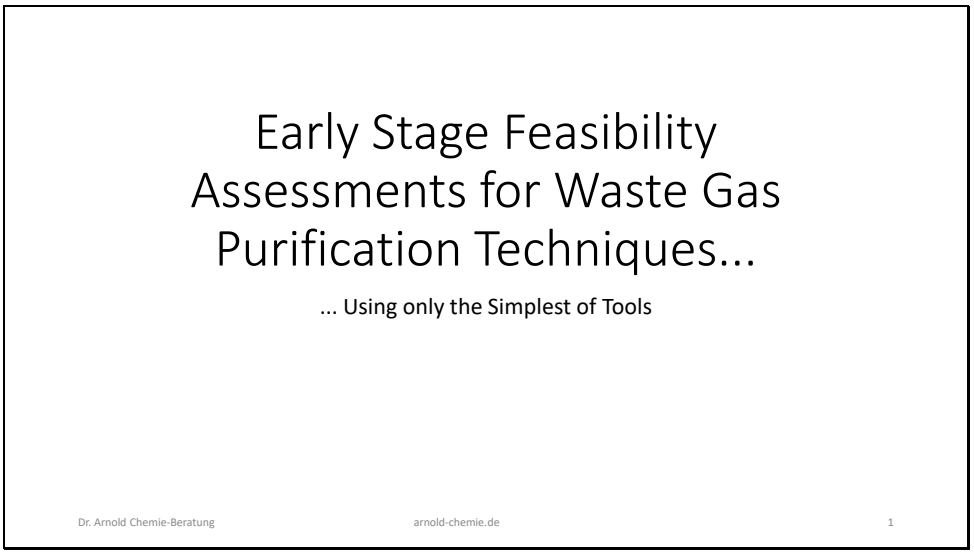
Slide 1



This is the long version of a presentation held at the 3P Adsorption week on April 15th, 2021.

In contrast to the general tone of the presentations, which were showcasing more and more sophisticated and high-tech analytical devices for adsorption measurement, I wanted to demonstrate how the pragmatic practitioner works: *At least in the early stages of a project, only the simplest, most cost-effective means are used.* Still, even then one does not want misleading results.

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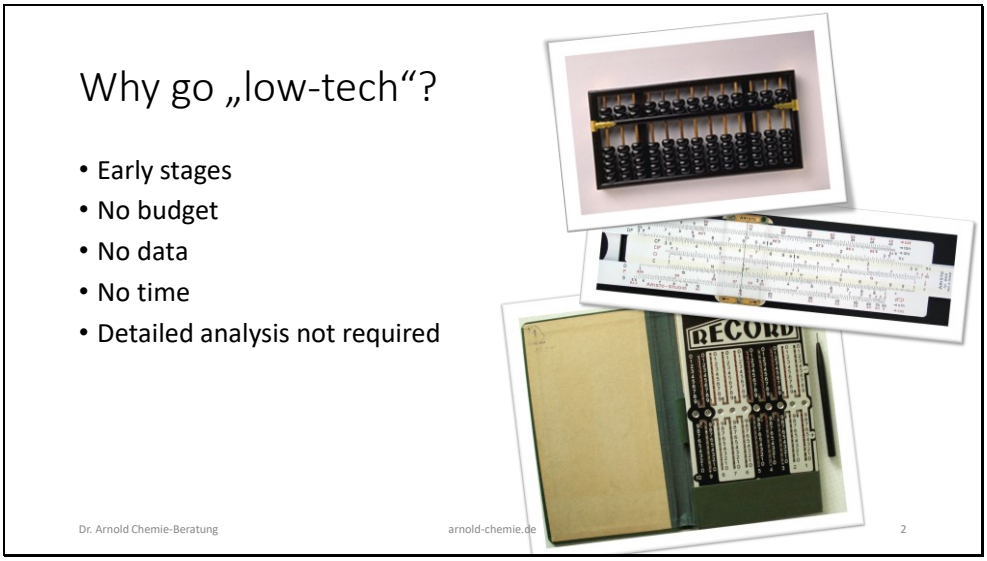
Slide 2



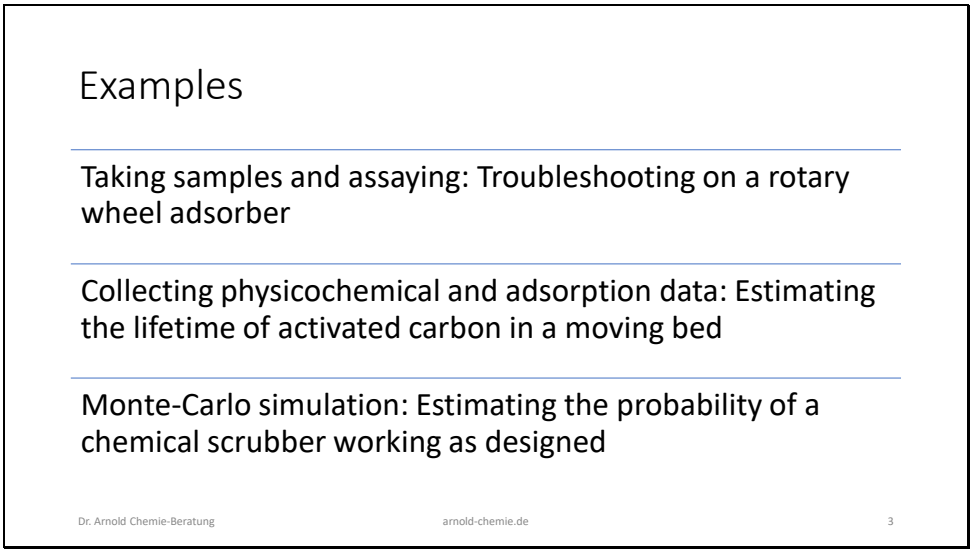
Seeing the gorgeous instrumentarium demonstrated during the last three days, *WHY WOULD ONE EVEN WANT TO GO LOW-TECH?* The answer is: In the early stages of a project, you cannot sell full studies. The customer is ok with limited insights at this point.

The situations comprise early stages of

- a feasibility assesment
- a trouble shooting project
- a measurement plan

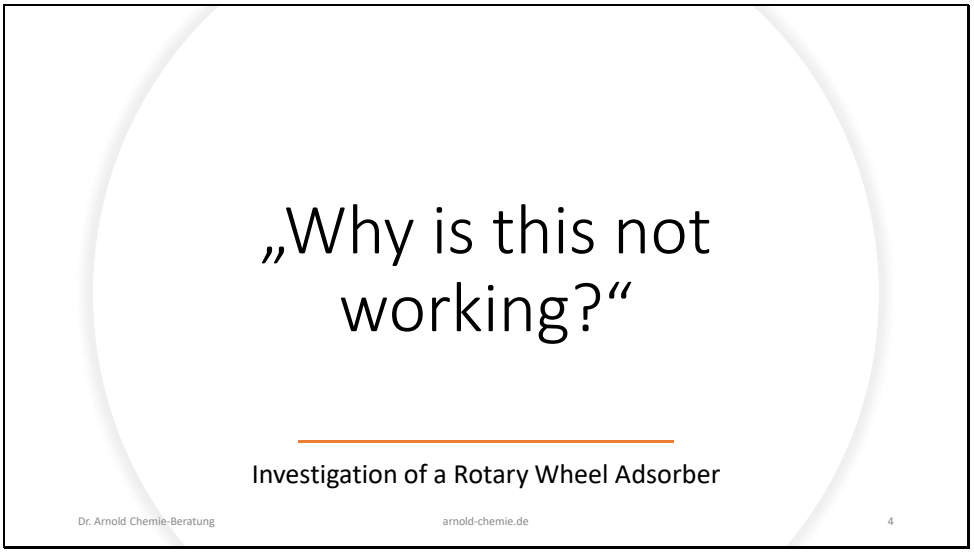
The question at this stage is mostly: „How can we even start to solve the problem?“

Slide 3



I have chosen three examples in which it was possible to make the first decisions spending only a few hundred Euros on assays and studies.

Slide 4



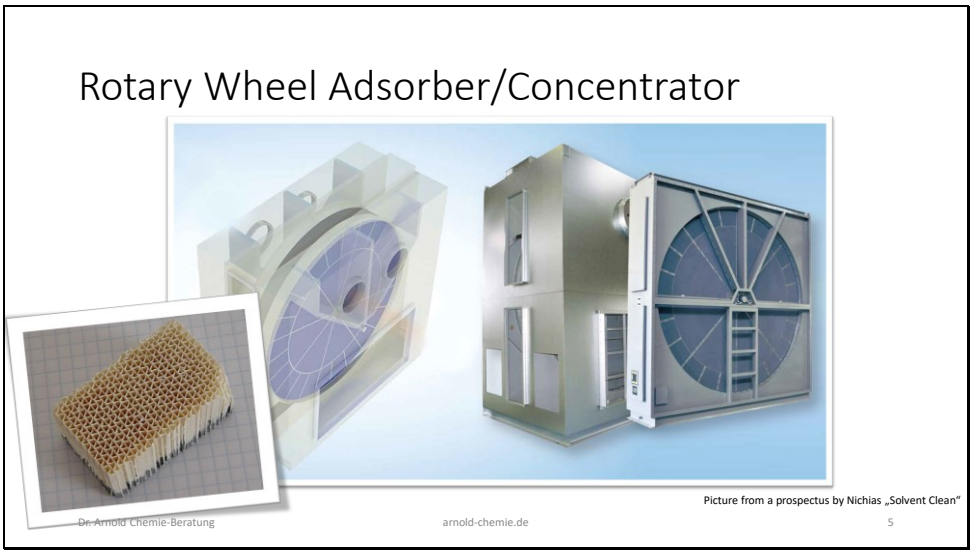
Rotary wheel adsorbers are notorious for the problems they can cause.

- Adsorption-desorption cycles, as a rather complex process, are known to cause all manner of trouble.
- One root cause is often the incomplete assessment of the waste gas situation.
- Also, adsorption processes are being viewed as „fixed recipes“ which are independent of the chemical nature of the adsorptives.

In this case, there were several rotary wheel concentrators in situations with complex waste gas compositions, with more than 50 different VOC present. The problems were (as always)

- reduced life time of the rotor
- exceeding the emission levels
- and in one case autoignition.

Slide 5

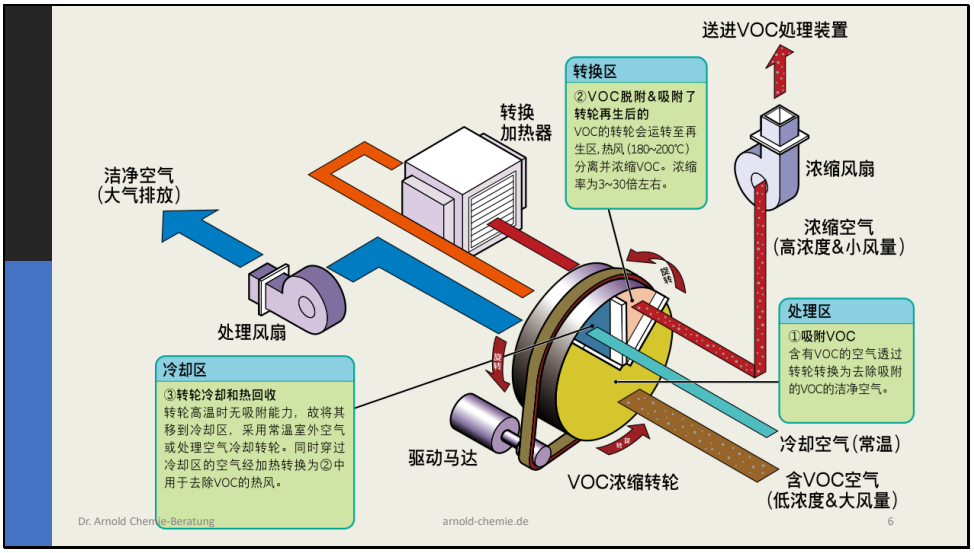


What is a rotary wheel adsorber?

These pictures give a general idea of the rotor itself. Airflow can range from 12.000 to 138.000 Sm^3/h. The smallest rotor would be 1,65 m in diameter, the largest 4,8 m, that is, two stories high.

The zeolite is dip-coated as a thin layer onto the ceramic or glass-fiber honeycomb, like shown in the inset picture (which is in reality a catalyst, note the black catalytic coat at the bottom of the sample, but the basic material is the same zeolite-coated honeycomb).

Slide 6



Process chart, from the prospectus of a Japanese manufacturer:

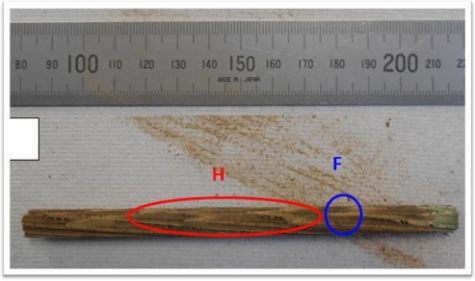
- The waste gas goes through the adsorption sector of the wheel (yellow) directly to the stack. Therefore, the adsorption process must meet emission threshold values.
- Desorption air gets preheated in the cooling zone (blue), gets reheated in the electrical heater and passes the desorption zone (pink) at around 200 °C. Sometimes deep cleaning – a hotter desorption cycle at around 220 – 230 °C without the presence of waste air– is performed. Higher temperatures than that are not possible because the elastomer seals would break down, even though the zeolite itself can be heated to almost 800 °C.
- The VOC concentrate – concentrated to anywhere from 1:6 to 1:20 or higher, depending on the waste gas composition - goes to some sort of aftertreatment. This is most commonly combustion in a catalytic or recuperative incinerator. In rare cases the concentrate is treated by condensation, in which case it would pass a recuperator.

Slide 7

Trouble to shoot

- Clean gas values rise
- Emission threshold values not met
- Self-heating during deep cleaning, development of smoke, autoincineration

➡ residue buildup



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What is causing the trouble?

- A sample was taken from the zeolite wheel with an instrument that roughly resembles an apple corer.
- Residue buildup is visible with the naked eye: Consider the tan color of the sample, as opposed to the original off-white of the sample on slide 5.
- Residues form due to incomplete desorption. Desorption is incomplete either because there are high boilers in the VOC mixture, with a desorption temperature well above the regeneration temperature, or because molecules decompose thermally on the zeolite before they have time to desorb. In most cases there is a combination of the two.
- In an ideal world, or if you want to meet the warranty conditions, only sufficiently stable solvents with a boiling point up to 150 °C would be concentrated on a rotor.
- Under realistic conditions a fraction of the organic matter will not be desorbed and turns to coke during repeated heating and cooling cycles. This crystalline form of carbon blocks up an increasing fraction of the zeolite pore systems, lowering the adsorptive capacity of the wheel.

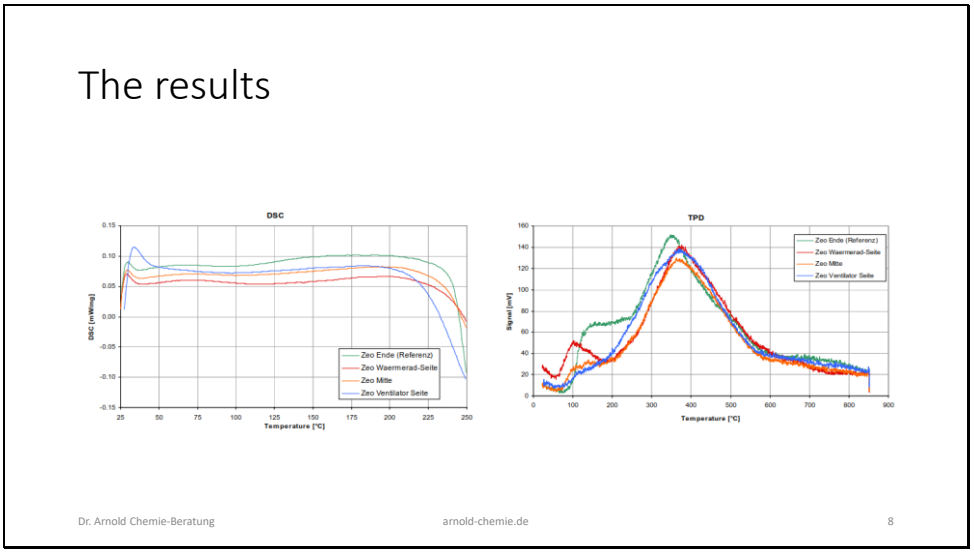
The customer asked: What can be done? The VOC composition will not change! Is there a way to operate the wheel to make it last longer than a few months?

My suggestion was:

- Find a feasible deep-cleaning regime. The manufacturer allows occasional heating to 230 °C, the limit due to elastomer seals.
- Perform a Differential Scanning Calorimetry DSC on used zeolite samples. This will tell us how high we can go temperature-wise without exothermy and thermal runaway occurring.

- Perform a Thermally Programmed Desorption TPD to find out whether a deep cleaning cycle is even worth it. Will there be sufficient desorption to justify the necessary downtime and the additional wear and tear on the rotor?

Slide 8



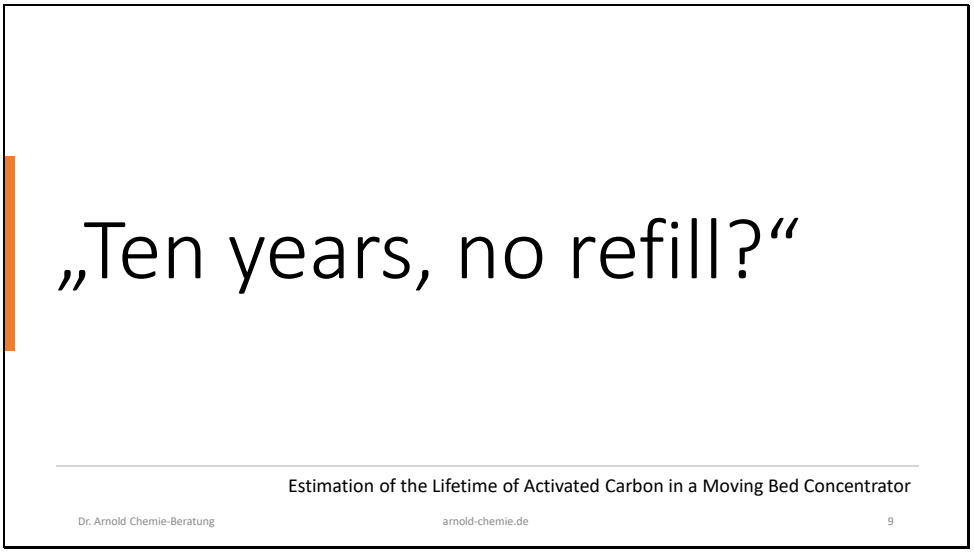
- *DSC* (left side) shows that heating above ca. 220 – 230 °C results in a strong heat effect, enough to cause thermal runaway (as had already happened once).
- *TPD* (right side) shows that especially on the entry side of the wheel (blue) every additional Kelvin helps with desorption.
- *Temperature measurements* directly at the wheel showed that during normal operations, the desorption temperature of 200 °C was not even reached. The effective desorption temperature was only 170 °C, so adsorbate buildup was fast.

We decided on a temperature regime for the new wheel which was then being installed:

- Desorption temperature should be at precisely 200 °C.
- Deep cleaning should not exceed 225 °C. As the desorption air stream goes countercurrent to normal flow direction, the entry side (which carries the greatest part of residues and had the lowest onset temperature for exothermal reactions) does not become overly hot.

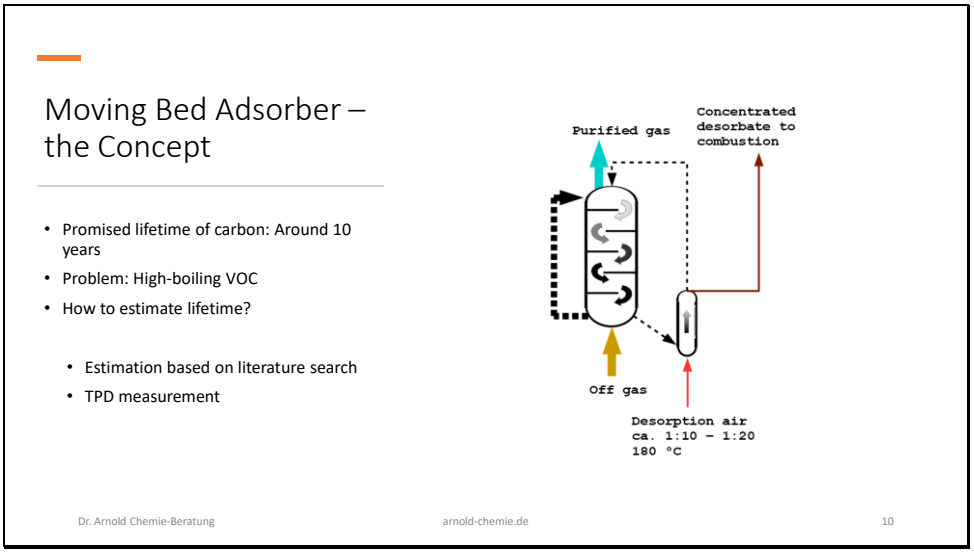
The new wheel has now been in operation for almost a year, with no signs of decline.

Slide 9



If something sounds too good to be true it usually is not true. Like having activated carbon remain in place for 10 years…

Slide 10



- Similar to a rotary wheel adsorber, this unit is a *CONTINUOUSLY OPERATING*, but *ACTIVATED CARBON-BASED CONCENTRATOR*. It consists of a moving bed adsorber with an airlift to transport

the granulated carbon back to the top of the column. A fraction of the activated carbon goes through a desorption unit instead of returning instantly to the column top. The desorbate goes to a small catalytic post-combustion unit.

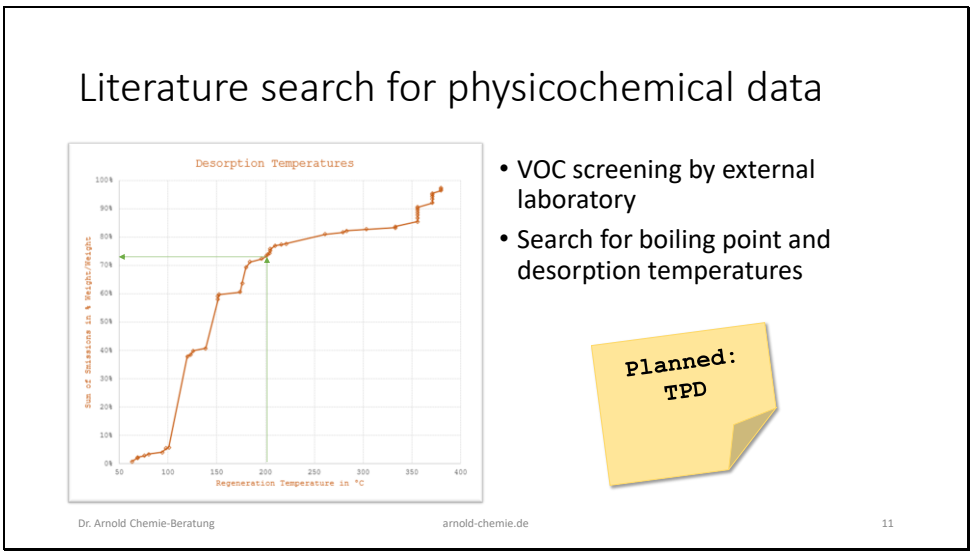
- A zeolitic rotary wheel had been ruled out already due to the presence of high-boilers. These accumulate on activated carbon, too, but changing activated carbon is not as aggravating as changing an adsorption wheel.
- The unit is very expensive – CAPEX is in the “n million €”-range
- Changing the activated carbon costs an estimated 50,000 €. One change per year would be considered appropriate. If, on the other hand, changing the activated carbon became necessary several times a year, costs would add up too much.

The customer asked: How long can we expect the activated carbon to last under our operating conditions?

My suggestion was:

- Find out from published adsorption data which fraction of the organic load can be expected to desorb, and calculate the life time of the activated carbon from there.
- Test it by using a sample of the original activated carbon, but in a stationary pilot scale unit. Then take out a small sample of the used carbon and do a TPD to determine what fraction of the substance is desorbed at which temperature.

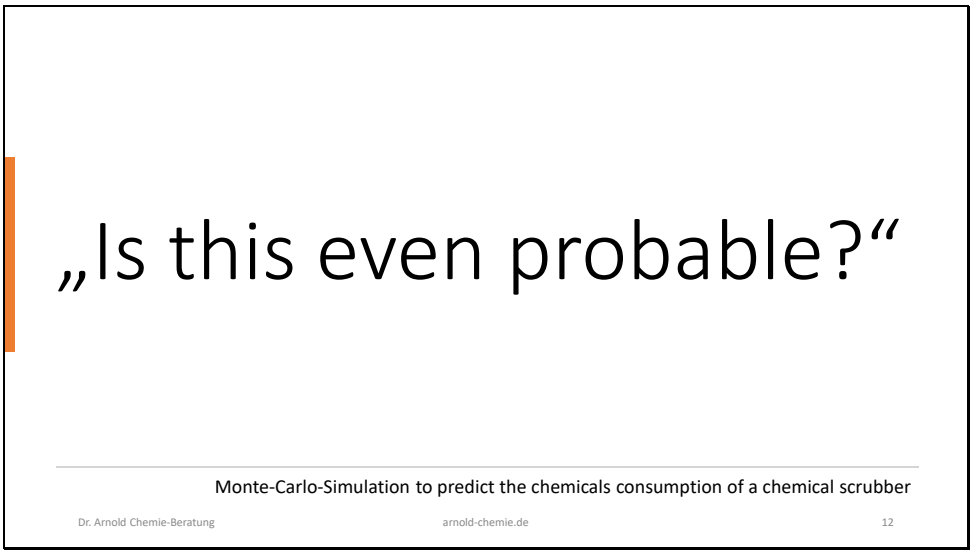
Slide 11



- Roughly 50 substances were identified by a GC (gas chromatography) screening and the chemical literature was scanned for data on their adsorption behavior toward activated carbon.
- This is of course generic and incomplete.

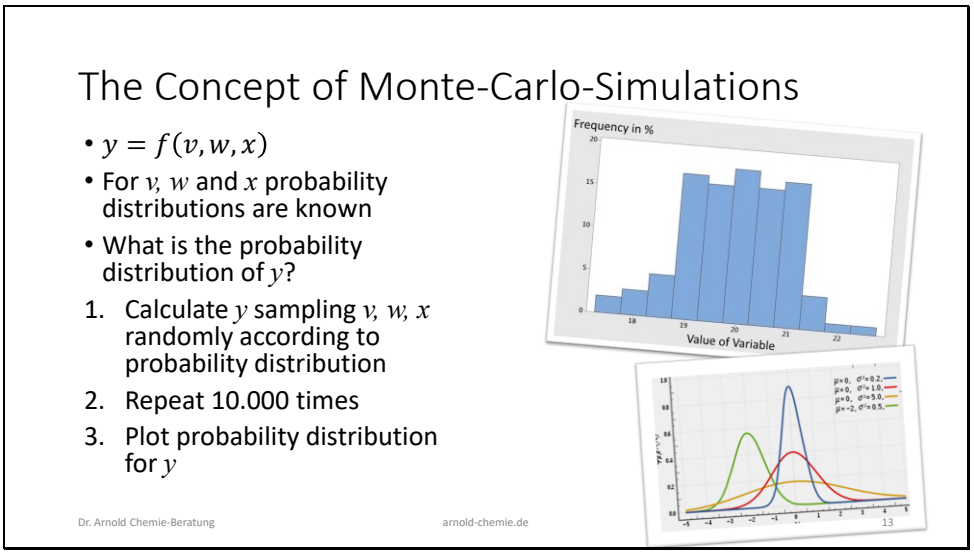
- Desorption at 200 °C (upper temperature limit) would desorb only around 72% of all the VOC present.
- The expected lifetime of the activated carbon shrinks to “several months”.
- This needs to be verified experimentally.
- Planned are static adsorption experiments on an original sample of the activated carbon and TPD. This pilot scale test is still running.

Slide 12



A pilot scale chemical scrubber was run for a few days and the results were not as expected. Namely, the consumption of the chemicals was much higher than calculated, so all the preliminary operating cost calculations were off. Was this only a fluke – or is something wrong with the scrubber?

Slide 13



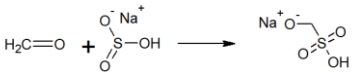
- Probability distributions can be measured histograms, Gaussian distributions, or shift with other variables, such as time.
- An algebraic solution for such cases is not accessible.
- Simple Monte-Carlo-simulations are often done in the financial sector. Probability distributions for variables such as economic growth, fund performance, inflation etc. lead to a probability distribution for earning or losing money with an investment.
- Monte-Carlo-simulations can be used whenever there is a complete equation with independent variables and known probability distributions for these.
- 10.000 as the number of runs is an arbitrary number, which depends on the system and how much is enough. Usually, it is noticeable when there are no more visible changes to the result with additional runs. Since for equations with only a few variables 100.000 repetitions take less than 300 seconds on an office computer, there is no need to economize.
- There are several commercial add-ons for Excel, or you can use “R”. The standard tools of Excel also allow you to perform Monte-Carlo-simulations, but this is much more complicated than working with an add-on.[1]

[1] I have tested several add-ons with this example, a description is on my blog, albeit in German: https://www.arnold-chemie.de/2020/03/monte-carlo-simulation-fuer-arme-teil-1/ and part 2 and 3 of the series.

Slide 14

The Oxidative Scrubber

- Scrubber for formaldehyde in oven waste gas
- Chemical system: Sodium bisulfite/sodium hydroxide forming non-volatile bisulfit adducts.



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- The picture shows the half-mounted pilot scale scrubber on site.
- The chemical reaction in the scrubber, called a bisulfite adduct formation, is fast and turns formaldehyde into a soluble, but non-volatile compound.
- An alkaline pH of 9 is needed for this chemical reaction.
- NaOH (sodium hydroxide, or caustic soda) and $NaHSO_3$ (sodium bisulfite) are added automatically, controlled by a pH electrode and a redox sensor.
- The consumption of NaOH was huge, much more than was predicted. As NaOH is a rather expensive base, the costs would add up over the long haul.
- Several fluctuating factors influence the NaOH consumption in a complicated way. Was the consumption within the range of what could be expected?

Slide 15

Which Variables Control the Amount of NaOH Added to the Scrubbing Solution?

Variable	Probability Distribution
Consumption through reaction with CO_2	Measured values/histogram
pH electrode drift due to temperature changes	• Measured values/histogram for temperature • Calibration function of pH electrode: Gaussian distribution of actual pH around measured value
Acetic acid in the oven gas	Measured values/histogram

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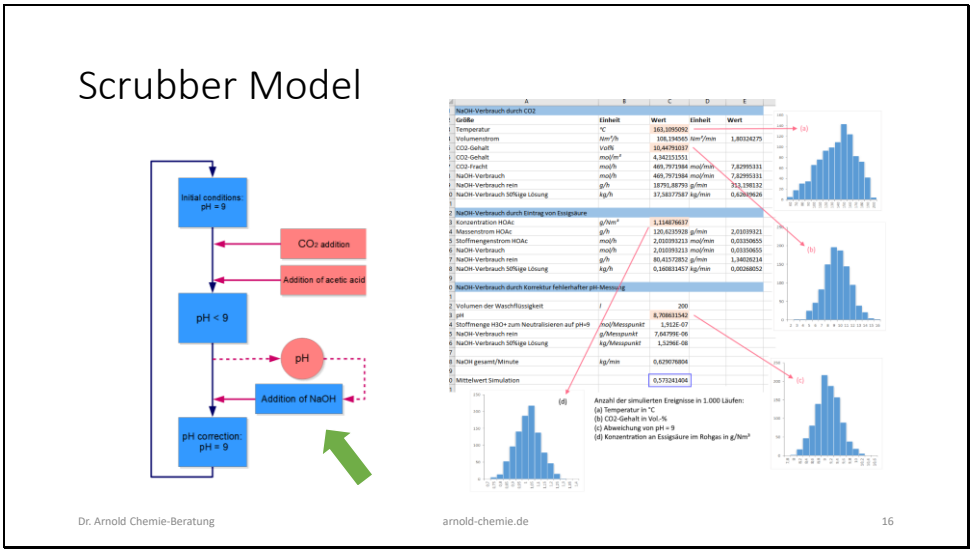
NaOH is added to the scrubber fluid automatically. The adjustment of the metering pump is influenced by several factors.

- While the bisulfite adduct formation does not use up any sodium hydroxide, it is needed to keep the pH at 9. *Sodium hydroxide is mostly used up by a reaction with carbon dioxide*, which is a considerable factor even at atmospheric conditions. Here, however, the waste gas was coming out of a directly fired oven and contained several percent of CO_2. The goods that were baked in this oven were loaded through a pair of doors which opened and closed regularly twice a minute, leading to strong fluctuations in the CO_2 concentration. For the variable “CO_2 concentration” longtime measurements were depicted as a histogram to be used in the simulation.
- The NaOH metering pump was directly controlled by a *pH electrode*. Of this, the output is *temperature dependent*. Normally it would have to be calibrated to the operating temperature. But this was not constant, because the scrubber was used as a temperature quench, too. The temperature was again depicted as a histogram, while the temperature-dependent error of the electrode was assumed to have a Gaussian distribution around a “real” pH.
- Besides carbon dioxide, the oven air contains other acidic VOC like acetic acid. From several analytical screenings a concentration distribution was constructed, though there were admittedly not enough measurements to make this accurate.

Slide 16



- The flow diagram on the left side shows how the influencing factors on NaOH metering come together.
- pH is mesured every minute, so every calculated loop also represents one minute.
- The quantity of added NaOH is calculated. Since the pH can become more alkaline than 9, this calculatory value is sometimes negative, though this has no physical meaning: In effect no NaOH is dosed for several minutes until pH catches up.
- The NaOH losses by scrubber fluid exchange are not calculated here since this is not done often. It could easily be figured in, though.

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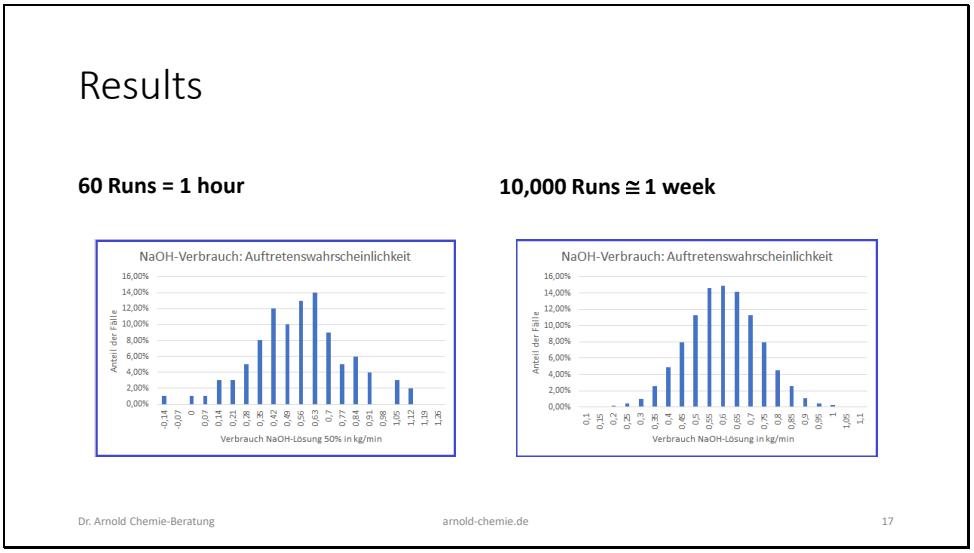
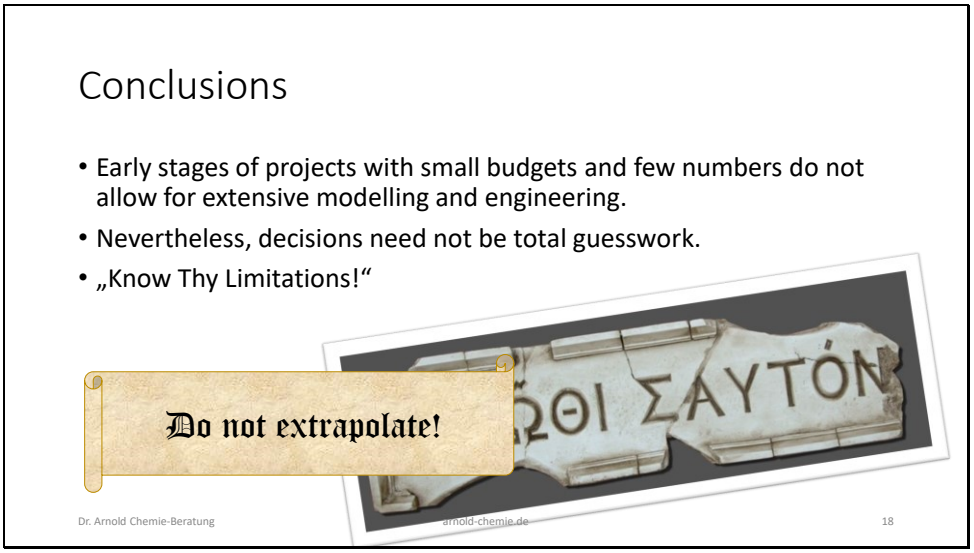
Slide 17



- The two histograms show the probability distribution of NaOH consumption, depicted as kg of 50% aqueous solution per minute.
- Two calculations were performed: With 60 runs, representing one hour, and with 10,000 runs which is approximately one week (10,080 minutes).
- After 10,000 runs the distribution is much smoother than after 60 runs, and the maximum has shifted to higher values.
- It is most probable that the scrubber will use between 0.55 and 0.65 kg/min 50% NaOH solution, which is 33 – 39 kg/h.
- In reality, it was using 50 – 60 kg/h!
- Since NaOH is expensive, and the resulting wastewater is very saline, it would pay to look for the defect or error in the measurement and control technology. Other error sources could be incorrect waste gas assessments, leading to unrecognized side reactions.

Slide 18



Like this beautiful fake antique relief which you can use to dress up your garden hut as the Oracle of Delphi says: „Gnothi seauton“ – know thyself, or in this case, know what you know, know what you don‘t know, measure what‘s essential, work with what you have and, whatever you do, never extrapolate.