LARGE SCALE CALORIMETRY

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This paper discusses the potential benefits to be gained from accurate measurement of the heat energy output from plant scale reactors. The incorporation of thermocouples and a flow meter into the vessel cooling system permits accurate measurement of the plant scale heat energy output rate and thereby provides an accurate measure of the accumulation of reagents at any given time. This procedure permits safer working and improved understanding of the chemical manufacturing process. The potential benefits from modification of plant scale reactors include a reduced number of incidents in the chemical industry together with improved optimisation of the process on the plant.

As above
Calorimetry, isothermal, heat-balance, heat-loss,

INTRODUCTION

Statistics show that the highest numbers of hazard and safety related incidents per specific chemical process occur with high energy systems, see “Chemical Reaction Hazards” by Barton and Rogers, reference 1. Specific reference is given to polymerisations, nitrations, and sulphonations, i.e. all highly energetic systems. It should be noted that less energetic systems could also give rise to significant chemical reaction hazards. The key feature is the amount of stored energy during plant processing, i.e. the product of potential heat energy release and accumulation. Further analysis shows that a lack of understanding of the balance between process heat energy output and available vessel cooling capacity is a major factor in many of these incidents. Process maloperations are responsible for the next highest number of chemical reaction hazards. Overall, it can be deduced that many parts of the chemical industry suffer from a lack of knowledge or appreciation of the potential heat energy output of a given manufacturing process and in particular of the kinetic parameters associated with the process, i.e. the rate of heat generation.

Highly energetic processes and other moderately energetic processes often have the potential for uncontrolled reaction to give rise to excessive heat energy output leading to vessel over-pressurisation and possible ejection of the batch from the reactor, etc. The consequence of runaway chemical processes can be very costly and can involve loss of life as well as loss of plant, loss of manufacturing capability, loss of morale, bad publicity, etc. As well as cost implications, legislative pressure from various government bodies requires that the chemical industry examine properly a proposed process to establish if it gives rise to a potential chemical reaction hazard and if so to determine safe operating conditions.

The most usual processing methodology is based upon semi-batch operation and the most usually Basis of Safety for a semi-batch chemical manufacturing process is based upon process control. Process control usually involves the controlled addition of a key reagent to the remaining materials whilst maintaining the batch at a given set temperature. To facilitate operation, many chemical manufacturers will pre-determine the rate of addition by examination of the proposed process in the laboratory using a calorimeter.

There are a number of commercial isothermal calorimeters available, for example the HEL Simular, Mettler Toledo RC1, etc. Furthermore, some companies have developed their own system, for example the power compensation heat flow calorimeter developed by Avecia, figure 1. Use of these calorimeters allows examination of a given proposed manufacturing process under the proposed normal operating conditions. Note: It is also possible to use the calorimeter to examine certain maloperations, for example rapid addition, omission of catalyst, etc.

The isothermal calorimeter produces a kinetic profile, i.e. process power output versus time, of the given proposed process. This data can be processed to allow determination of the required vessel cooling system for a given addition rate or vice versa. From a hazards viewpoint, the data can be used to determine if there is a build up or potentially dangerous accumulation of reagents and therefore if the process gives rise to excessive amounts of stored potential energy. As a result of the calorimetric analysis in the laboratory, the proposed process may be revised to avoid a potentially dangerous accumulation of reagents. Once a process has been examined and safe-operating conditions defined, it is possible to consider the scale up of the process to a manufacturing scale. This procedure of examination of a proposed process in a calorimeter prior to operation on a manufacturing scale is in common use throughout the chemical industry. It should be noted that the isothermal calorimeter represents only one component of a more comprehensive package of experimentation, which may be used to examine a given proposed process. Never the less the isothermal calorimeter is most frequently used to determine the required vessel cooling system for a chemical manufacturing process.

The use of calorimeters has improved the safety performance of the chemical industry. However and despite increased availability and use of calorimeters, the chemical industry still suffers from an unacceptably high number of incidents, which are due to excessive and often unexpected heat energy outputs from a given chemical processing system. The archives abound with such examples. As an example and typical of the unexpected behaviour that can occur in a chemical manufacturing process, a minor incident occurred during a pilot scale reductive acylation which was being operated by a UK chemical manufacturing company.

CASE HISTORY

A typical chemical manufacturing process incident was the subject of an earlier paper, reference 2. A brief synopsis of the incident is provided below to illustrate the need for accurate measurement of the heat energy output from larger scale reactors.

The process had been examined, using heat flow calorimetry, prior to the start of manufacture and safe-operating conditions had been established. The process had been operated for several years without incident and was considered safe and robust.

The process itself required the addition of an aromatic nitro body to an agitated batch comprising an anhydride and acid together with finely divided iron. Calorimetric examination had established the reaction kinetic profile and a suitable addition regime had been established, see figure 2.

The chosen basis of safety was process control requiring addition of the nitro body to the batch over a minimum number of hours whilst maintaining the batch at a given set temperature. The processing methodology was considered safe and had been operated many times always giving the product in good yield and quality and without giving rise to a chemical reaction hazard. The process was considered robust.

The incident batch occurred at the start of a new campaign in which a different grade of iron was being used. In fact the new grade was more finely divided and was considered to be of a higher specification than the earlier grade, which had been used successfully for many years. Charging of the batch was carried out as usual and there were no indications that anything unusual was occurring. The operator had recorded that the start of the addition of the nitro species had been accompanied by a temperature spike, which was the normal observation. The addition of the nitro body was completed over the normal period to the batch at the given set temperature. The were no further temperature deviations. In accord with normal practice at the end of the addition the batch was sampled for analysis. Analytical results were available within about 30 minutes and indicated that the reaction was only 10 to 20% complete. Coincident with the obtaining of the analytical results it was found that the pilot scale batch was self-heating at a rapid rate. The batch self-heated to boil and thereafter to eject a considerable portion of the batch from the reactor. The details of the incident batch, i.e. the time temperature profile, are shown in figure 3.

The incident was minor in nature, mainly due to small scale of operation, but it does serve to illustrate that despite the best of intentions and the use of modern sophisticated calorimeters incidents still occur.

A detailed and extensive investigation into the incident batch was carried out and the cause of the incident was found to involve the use of the new “improved” grade of iron. The finely divided iron was shown to have an extensive surface coating of iron oxide, which in practice prevented the desired reductive alkylation from occurring. It is worth noting that the surface coating was not comprehensive and some of the iron was active. The active portion produced a temperature kick, which the operator took to indicate that the process was progressing in the normal manner. Once the non oxide-coated material had been consumed the bulk inactive material failed to react with the nitro body, which was being charged in a controlled manner. Thus despite charging the reagent in a controlled manner, a potentially dangerous “All-in” batch was generated. With time the oxide layer was removed by the acid, i.e. pickling, and the “All-in” batch reacted with the consequence detailed above.

The process was re-examined in a heat flow calorimeter using the new grade of iron, see figure 4. Addition of the nitro body was carried out over five hours to the batch at 25°C. The process power output profile shows the accumulation of reagents and subsequent resultant very rapid reaction, which overwhelms the reactor cooling system. Analysis shows that about 80% of the total process power output occurs after the addition of reagents is complete. The initial part of the reaction is comparable to the earlier calorimetric data confirming the presence of some normal active iron.

The above small scale minor incident is typical of the scenario which can affect many chemical manufacturing processes. The lack of accurate measurement of heat energy output from larger scale reactors, and in particular plant scale reactors, has led to many serious incidents in the chemical industry. It is the purpose of this paper to highlight the potential dangers and to propose safer working practices.

Controlled Additions

It is worth considering what is meant by controlled addition. Frequently a Basis of Safety will call for the addition of a key reagent to be made to the batch in a controlled manner whilst maintaining the batch at a given set temperature. In general it is assumed that the batch will behave in a similar manner to the laboratory calorimeter experiment and that the addition procedure will avoid any potentially dangerous accumulation of reagents. As shown above this hypothesis can be wrong.

Furthermore, consider a simple yet frequent maloperation of failure to charge a catalyst at the start of processing. The above precaution, i.e. add at a rate balanced to cooling, has little, if any benefit and affords no protection to the plant and operators. In the event of omission of a key catalyst the subsequent addition of reagents would be carried out with little, or no, process heat energy output and would generate a batch, which apart from catalyst could be considered to be “all-in”. There are many examples of such batches suddenly and without warning undergoing rapid reaction leading to serious chemical reaction hazards. However, the identified safety precautions had been followed and the reagent was charged in a controlled manner to the batch at the given set temperature.

In the above nitro reaction process, to provide a means for future safe operation it was decided to revise the addition procedure such that the nitro body would be charged to batch portionwise with analysis of the batch prior to each subsequent addition. The next aliquot addition would only be carried out provided that the previous analysis had proved that there was an acceptable level of reagents present. In this way it was possible to identify if a potentially dangerous accumulation of reagents was present in the batch prior to the continued addition of the key reagent.

The revised processing methodology did provide a means of ensuring safe operation but was time consuming and the required analysis was costly. Such procedures were thought necessary to prevent a reoccurrence of the incident. However, alternative safe practices were not readily available.

Large Scale Calorimeter

It is recognised that it is often impractical to provide controlled additions of energetic reagents together with frequent analysis of the progress of the reaction. One alternative has been introduced within Avecia with some expected success as well as unexpected benefit to the business.

A plant scale reactor within Avecia has been modified to incorporate a pair of matched thermocouples into the vessel cooling system, i.e. to measure the difference in coolant temperature of the fluid entering and exiting the vessel jacket coolant system. A flow meter provides an accurate measure of the rate of flow of coolant through the vessel jacket. A third thermocouple monitors the batch contents temperature. The data is then processed according to heat flow and heat balance principles.

In one example, the reactor was used to carry out a manufacture involving a highly energetic metallation of a reactive organic compound via an organometallic species. The process was examined in a laboratory-based calorimeter and the heat of reaction determined and the kinetic profile of the reaction established under normal operating conditions, see figure 5. A Basis of Safety was written and the associated precautions were incorporated into the works process operating instructions.

The process was operated on a plant manufacturing scale using the modified reactor as described above.

The progress of the process reaction on the plant was followed using the various thermocouples and coolant flow meter. Figure 6 shows the process operated with batch temperature control at -40°C. The addition was completed in two hours and the batch temperature was maintained at about -36°C to -39°C. Note: The coolant temperature dropped from -40°C at the start of the addition to a minimum value of -68°C during the addition. Once the addition was completed, the vessel coolant temperature returned to the jacket temperature, i.e. within about 45 minutes after the addition was completed. It can be seen that the addition is immediately exothermic and that a small accumulation of reagents is generated. Analysis provided an accurate thermodynamic profile of the progress of the process. Two techniques were employed, i.e. heat balance calorimetry and heat flow calorimetry.

Heat Flow Principles

Heat flow calorimeter depends upon knowledge of the heat transfer coefficient of the batch/vessel together with the temperature differential between the batch and the jacket cooling system.

$$\text{Rate of Process Energy Output} = UA(T_b - T_j)$$

where:

U is the heat transfer coefficient of the batch / reactor
A is the available vessel / jacket cooling area
Tb is the temperature of the batch in the reactor
Tj is the temperature of the coolant in the vessel jacket

Heat Balance Principles

In heat balance calorimetry a differential thermocouple, or a matched pair of thermocouples, is used to provide a measure of the heat energy gained by the fluid passing through the vessel cooling system, i.e. the process heat energy lost from the batch to the vessel cooling system. The product of the coolant temperature differential, i.e. the difference between the cooling fluid temperature entering and leaving the vessel jacket cooling system, and the coolant flow rate will provide an accurate measure of the rate of heat dissipation from the batch to the coolant system.

Rate of Process Energy Output = (T_{J2}-T_{J1}) x Flow rate x Specific Heat of the Coolant

Results

The results of the analysis were very encouraging and both heat flow and heat balance analyses were consistent with the data obtained from the experimental scale isothermal calorimeter, which operated, by power compensation heat flow calorimetry..

Analysis of the proposed process using the laboratory based isothermal power compensation calorimeter had indicated that the heat of reaction associated with the addition of the key reagent was -15 k calories per mole of reagent.

Heat flow analysis of the plant scale process indicated that the manufacturing scale heat of reaction value was -14.1 to -15.2 k calories per mole. Furthermore the peak power output in terms of Watts of heat energy evolved per unit mass were very comparable between the laboratory based isothermal calorimeter and the modified plant scale reactor.

Overall, a number of batches have been monitored and the results are very consistent. It is reassuring to know that the laboratory calorimeters can, if used properly, provide an accurate measure / model of the energy profile obtained in a plant scale manufacturing reactor.

Benefits

Increased Efficiency: Processes can be monitored to ensure that the addition profile is matched to the available vessel cooling system. In practice, with notable and well-publicised exceptions, most processes operate well within the available vessel cooling capacity. This can mean that addition periods are unnecessarily extended. In the example above, the addition rate has been modified, i.e. increased, such that there is a time saving of about 20% by comparison to the original plant operation.

Improved Safety: Continued analysis of the progress of a reaction allows the ready identification of any potentially dangerous build up of unreacted reagents. Note: It is possible for the analysis to be carried out on line and therefore the chemist or plant operator can readily determine the progress of a reaction at any time.

Increased Confidence: Confidence in operating the process is increased. Continual evaluation of the process heat energy output together with knowledge of the progress of the addition permits analysis to ensure that a potential hazardous build-up of reagents does not occur. Under such circumstances the addition of further reagent is suspended and technical advice is obtained.

Optimised Cooling Efficiency: A further unexpected benefit has been forthcoming in that analysis of the batch / vessel heat transfer proprieties has shown that the cooling system is more efficient at certain temperatures. It had been thought previously that improved cooling would be achieved by reducing the coolant temperature to a minimal value. In practice the calorimetric analysis has shown that improved cooling is achieved by the use of coolant at a specific temperature value at which the characteristics of the coolant system are utilised to their full potential. This has enabled the batch time to be reduced with the consequential gain in production and therefore manufacturing costs have been reduced.

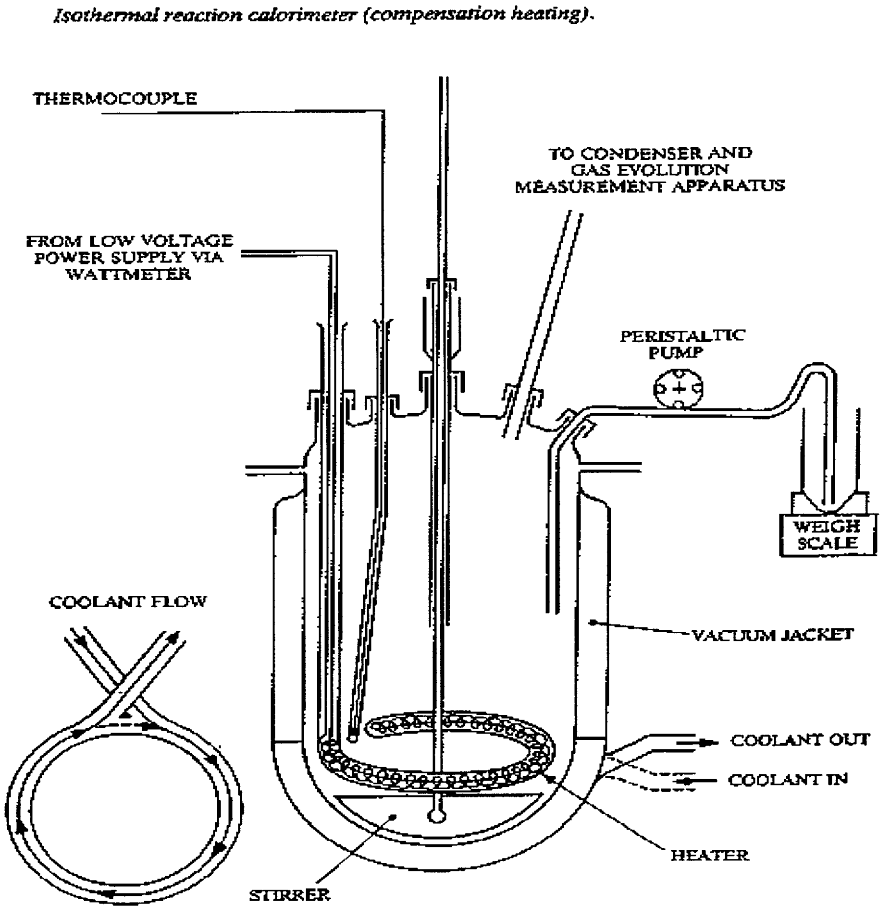
Conclusions

Overall, the incorporation of heat flow and heat balance analysis into the plant scale manufacturing capability has provided a step improvement in the safety of our plant. The accurate matching of reagent addition rate to the available vessel cooling system is apparent. Furthermore the matching of the addition rate to the amount of accumulation of reagent in the batch allows safer working and reduced risk of a serious chemical reaction hazard associated with operation of our processes.

References:

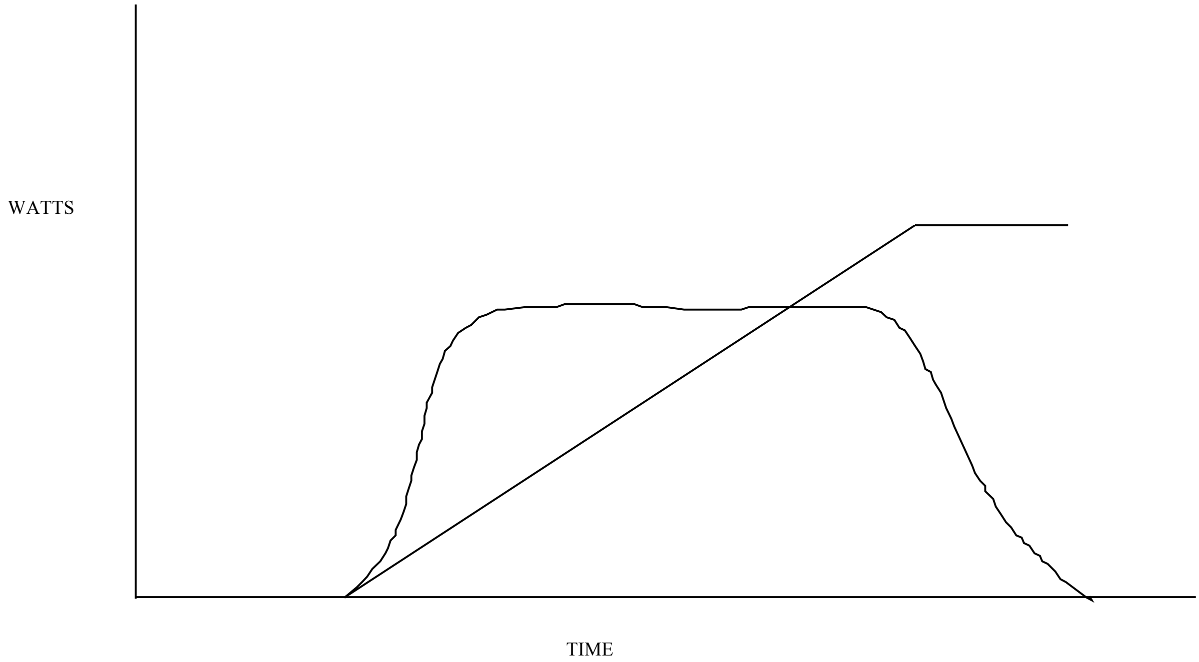
1. Barton and Rogers
2. PJ Duggan Hazards XIII

Figure 1: Power Compensation Isothermal Calorimeter as used in Avecia.

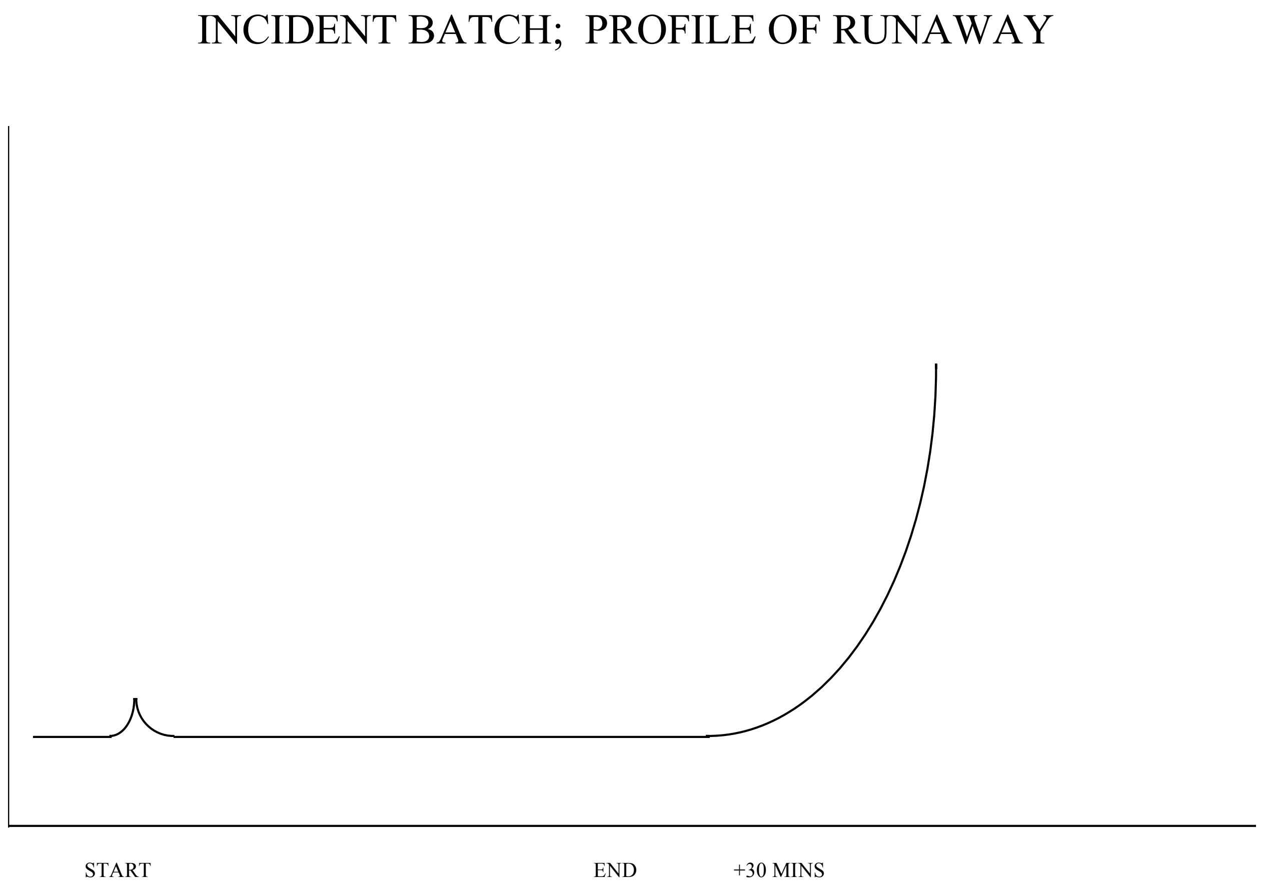


Incident process normal profile:

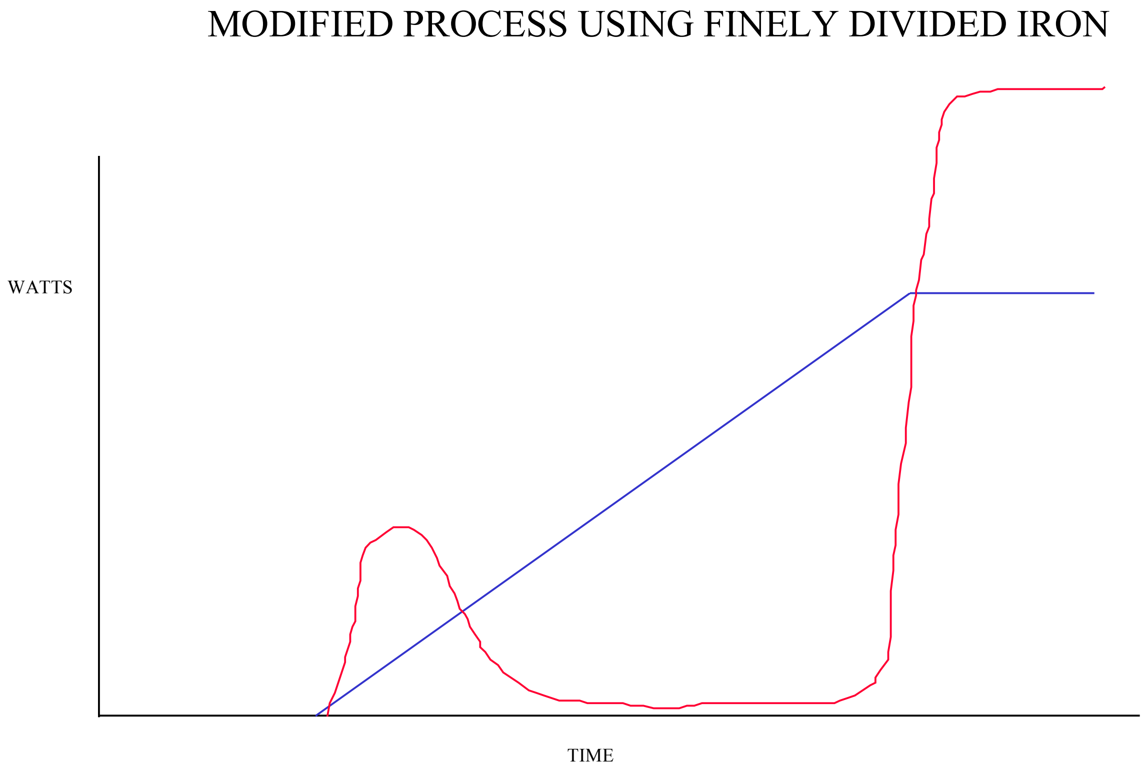
ORIGINAL PROCESS GRANULAR IRON



Incident batch: profile of runaway:

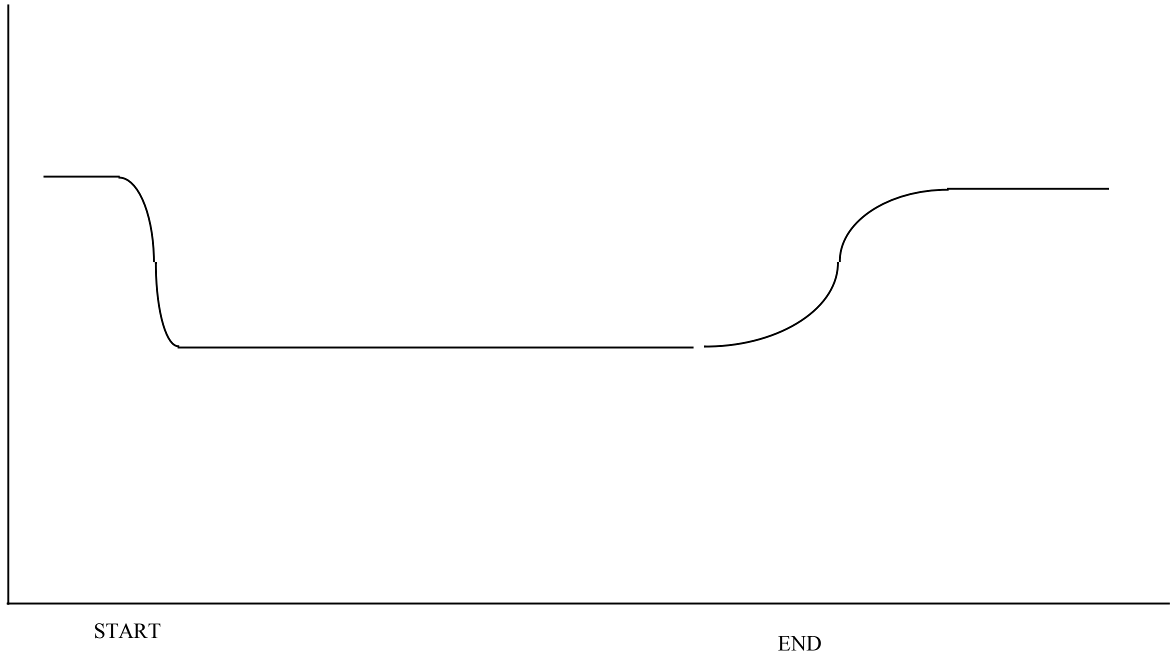


Isothermal Calorimetry: of Incident Batch



metallation Profile:

METALLATION PROFILE IN HEAT FLOW



Metallation with Batch Temperature Control at –40 °C